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PHOTODEGRATION OF METHYLENE BLUE AND TANNERY WASTEWATER BY C, N CO-DOPED TITANIUM DI-OXIDE

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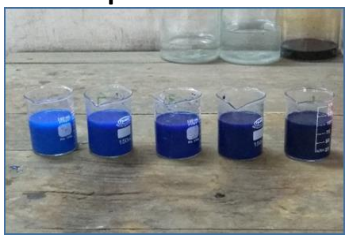
Graphical abstract



Abstract

Water is the most essential part of biological life but it is often contaminated by dyes and causes aesthetic problems in addition to health effects. The scarcity of clean water is on increase. Ultrasonic procedures, ozonation, electrochemical treatment, membrane separation, adsorption, and photocatalysis are the modern techniques used in separating dyes from water. Most of these techniques have limitations, but the use of semiconductors in decolorization through photocatalysis has attracted the interest of researchers as an ecologically benign and cost-effective strategy. Titanium dioxide was used as a photocatalytic degradant having a band gap of Eg 3.2 eV. Doping is an effective method for narrowing the band gap of TiO_2. In this study, an N and C co-doped TiO_2 was used and the samples were placed in a UV chamber for photodegradation. Primarily, the technology was tested for Methylene Blue and after that, for the dismounted wastewater from Tannery industries. Primary and secondary filtering were done for both the Methylene Blue and Tannery wastewater. Primary filtering was done using normal filter paper and secondary filtering was done using a Sterile Syringe Filter having a 0.45µm PES. Photocatalysis using co-doped TiO_2 in MB and wastewater has been demonstrated for various concentrations. Color removal of low-concentrated MB was more satisfactory than that of the higher concentration. The absorbance of the higher concentration of Methylene Blue showed significant errors. The color removal efficiency of TiO_2 for Tannery wastewater was moderate.

Keywords: dyes, photocatalysis, semiconductors, doping, photodegradation

1.0 INTRODUCTION

The leather industry, which is ranked fifth in terms of export-earning sectors, has been identified by the government of Bangladesh as having significant growth and investment potential. The major industries with the highest water consumption rates are tanneries. The disposal of the dyeing operation's effluents, whose function is the chemical fixing of colors on the fibers, frequently results in the coloring of tannery effluents. This colorful wastewater is a significant cause of pollution, algae blooms, and disruptions to aquatic life within the environment (Paul, 2013). Methylene Blue (MB) is used to tone up the colors of silk in addition to dying paper and office supplies. It has primarily been utilized for a number of therapeutic and diagnostic operations in both human and veterinary medicine. Due to its complex aromatic compounds, hydrophilic nature, high stability against temperature, light, water, chemicals, etc., it cannot be degraded through the traditional water treatment procedure and may significantly pollute the environment. One of the best methods for methylene blue degradation is thought to be photocatalytic oxidation (Hou *et al*. 2018). TiO_2 was discovered to be a useful photocatalyst in the early 1960s (Fujishima, 2000). It can occur as an amorphous layer as well as in three other crystalline phases, including rutile (tetragonal), brookite (orthorhombic), and anatase (tetragonal) (Hasan et al. 2008). Titanium dioxide (TiO_2) is the most extensively used photocatalyst due to its high chemical stability, availability, and low cost (Tayade *et al*. 2009). The Honda-Fujishima effect was discovered, which resulted in the realization of the high reduction and oxidation

power of photo-excited titanium dioxide (TiO_2). Fujishima described the photo-induced breakdown of water on TiO_2 electrodes in 1972. Interest in environmentally friendly applications has grown since Frank and Bard initially investigated the potential of utilizing TiO_2 to break down cyanide in water. Titanium dioxide's surface photocatalytic reactions have received a lot of interest (Song et al. 2007). The synthesis of mesoporous titanium dioxide (TiO_2), the use of various TiO_2 morphologies (nanotube, nanowires, and nanospheres), lowering aggregation in NTO powders, and surface treatments of NTO are recent initiatives to improve the photocatalytic properties of NTO (Nanocrystalline Titanium Dioxide). To produce TiO_2 photocatalysts with increased photocatalytic activity, mesoporous NTO must be synthesized (Lazar et al. 2012). In terms of surface area, the impact of particle size on photocatalytic activity may be defined (Xu et al. 1999). Smaller particles typically have more surface area, which results in more activity. This can be explained by an increase in the number of active sites per square meter and by the pollutants' increased capacity to adsorb on the surface of the catalyst (Thiruvenkatachari, 2007). After 2000, doping TiO_2 to boost absorbent capacity became popular. Due to its large band-gap energy, TiO_2 application has a major disadvantage. There are many nonmetal and nonmetal compounds that can be used as doping agents. As an example, consider the following: nitrogen (N), sulfur (S), phosphorus (P), carbon (C), boron (B), fluorine (F), iodine (I), etc (Zaleska, 2008). TiO_2's band gap energy (3.0-3.2 eV) necessitates UV light irradiation. In a TiO_2 nanocrystallite, an electron-hole pair is produced by an ultraviolet photon with energy larger than Eg. These charge carriers may decrease or oxidize adsorbed molecular species if they diffuse to the crystallite surface before recombining. The total mineralization of existing contaminants would be the end aim (Yu et al. 2002). As a result, much effort has been expended in developing a TiO_2 photocatalyst capable of efficiently using UV light (Valdes, 2010). A few approaches have been explored up to this point, along with the doping of TiO_2 with transition metals, the synthesis of reduced forms with TiO_2-x structure by plasma treatment (i.e., formation of oxygen vacancy) anchoring organic dyes onto the surface of TiO_2, and the doping of TiO_2 with anionic nonmetals. Nonmetal dopants, such as C, N, S, P, and halogen atoms, may be more appropriate than other methods for extending TiO_2 photocatalytic activity into the visible region because their impurity states are near the valence band edge, but they do not act as charge carriers, and their role as recombination centers may be reduced when compared to metal cation doping. Nitrogen- and carbon-doped TiO_2 nanomaterials have been discovered to have better photocatalytic activity under UV light when compared to all other nonmetal-doped TiO_2 materials (Schneider, 2014). Recently, the simultaneous doping of two different types of atoms into TiO_2 has gained a lot of interest since it can produce different properties and a higher photocatalytic activity than just doping in a single element. For instance, Li *et al*. (2007) showed that TiO_2 nanomaterials co-doped with nitrogen and fluorine showed better visible-light photocatalytic properties than TiO_2 doped individually with those elements. This can be attributed to the synergistic impact of co-doping two elements, where the doped N atoms enhanced the absorbance and the doped F molecules increased surface acidity and reactant adsorption. Cong *et al*. (2006) developed C-N-TiO_2 nanoparticles via a microemulsion-hydrothermal technique, and then simply investigated their formation and photocatalytic performance. Their synthesis process also had several drawbacks, such as high cost, low yield, use of an organic solvent, etc., which delayed the practical application of TiO_2. However, they did not go into great detail about the explanation for the rise in photocatalytic activity. As a result, the purpose of this study is to explore the workability of C-N co-doped TiO_2 in the color removal effectiveness of Methylene blue at various concentrations, exposure durations, and Tannery discharged effluent using photocatalytic technology with a UV chamber.

2.0 METHODOLOGY

2.1 Materials

Here, TiO_2 bought from the local market was used as the photocatalyst to conduct the photoreaction. The band gap of TiO_2 has been reduced by doping TiO_2 with N and C. For nitrogen, urea was used and graphite was used as a carbon source. The method was applied to MB solution and tannery wastewater to reduce the absorbance of the solution. Two stages of filtering have been conducted. Firstly, by Whatman Grade 1 qualitative filter paper and secondly, by VWR international sterile syringe filter of 0.45 µm. The absorbance was determined by a UV-vis spectrophotometer (UV-2600 plus). Several concentrations of solutions have been made to compare the absorbance and color removal efficiency. The additional equipment used in the experiment are mortars, pestles, a magnetic circulation machine, an analytical balance, beakers, and glass rods.

2.2 Experimental Procedure of Methylene Blue

Titanium dioxide (TiO_2) was doped with 2% Nitrogen and 2% Carbon. For Nitrogen, urea was used which has about 50% Nitrogen by its weight. Graphite was used as a carbon source. This doping process was done with the help of mortars and pestles. A mixture of 2% graphite and 4% urea of titanium dioxide weight was produced. This mixture was grounded for about ten minutes for homogeneous mixing.

Different concentration of Methylene Blue solution was prepared for photocatalytic degradation testing. The solid powder was used as a source of methylene blue. The required amount of solid MB powder was measured with an analytical balance. The mixture of MB solution with TiO_2 was stirred in a magnetic circulation machine for ten minutes for homogeneous mixing. Then the MB mixture solution was placed inside the UV chamber at a pre-determined time interval. After taking out the solution from the UV chamber, solution was filtered using Whatman Grade 1 qualitative filter papers and also by VWR international sterile syringe filter 0.45µm and absorbance of methylene blue solution was obtained by using UV-vis spectrophotometer. This was the absorbance before photodegradation by titanium dioxide.

2.3 Experimental Procedure of Tannery Wastewater

Tannery wastewater contains a huge amount of suspended solids and deposited particles. To get the actual color of the

wastewater, filtering was done in two stages. Primary filtering was done with Whatman Grade 1 qualitative filter paper. Secondary filtering was done with a VWR Sterile Syringe Filter of size 0.45µm. The wastewater was filtered twice, before and after the photodegradation and in both cases, primary and secondary filtrations were carried out. The preparation of TiO_2 was similar to the experimental procedure of MB.

The color of tannery wastewater was measured with a spectrophotometer in the Pt-Co unit. The color was determined before and after photodegradation for comparison. Thereafter, the electrical conductivity and pH of the tannery wastewater were measured by an EC meter and a pH meter respectively.

3.0 RESULT AND DISCUSSION

3.1 Photodegradation of Methylene Blue

The absorbance of methylene blue was obtained using a UV-vis spectrophotometer at a 664nm spectrum wavelength. The absorbance at time zero indicates pure methylene blue without any action of TiO_2. Several absorbances of methylene blue were taken with respect to exposure times of solution in the UV chamber. The visual representation of color removal of MB has been demonstrated in figure 1. The absorbance of MB solution decreases with the increase in exposure time of UV light, which is shown in figure 2. But the decreasing rate of absorbance is slow. This experiment was done without filtering the final solution after UV light exposure, which might have lowered the degradation rate of the methylene blue solution. The solution was placed inside the UV chamber using test tubes, which can potentially reduce UV light exposure to the solution. Absorbance degradation was 15.4%.

The absorbance of 0.1ppm and 1.0ppm Methylene Blue is compared in figure 3. Both absorbance-decreasing rates are slow as the final solution was not filtered. Absorbance degradation of 0.1ppm MB was 26% and 1ppm was 26.26%.
The absorbance of the higher concentration of MB and higher exposure time showed a decreasing trend in figure 4. The degradation rate was 2% for 2.5 ppm, 5 ppm, 10 ppm, 40 ppm but 20 ppm had 7% degradation. The presence of suspended particles may be responsible for scattered values that cause interference with absorbance. Exposure to UV light may not be as good as it should be because the test tube was used in this experiment to keep the MB solution inside the UV chamber. In addition, a higher concentration of TiO_2 was used, but filtering of the solution after UV light exposure was not performed. The filtering of the solution after UV light exposure can help to get better color removal efficiency because the distance between the UV chamber and UV-vis spectrophotometer was about 120m and the suspended particles (C, N co-doped TiO_2) cause the disturbance due to travel distance. If the filtration after photodegradation could be done then the suspended particles would be removed and color removal efficiency would be better.

Filtering the Methylene solution after UV light exposure significantly improves photodegradation which is shown in figure 5. Filtering was done in two steps. Firstly, with normal filter paper, which is used in the TDS experiment. Secondly, with 0.45µm filter paper. In this experiment, 0.5g/L C-N co-doped TiO_2 was used. With the increase of exposure time in UV light, the absorbance of Methylene Blue reduces. 30(mg/L) had a degradation of 78%. The rate of degradation reduces as the concentration of MB increases. 300(mg/L) had 22% absorbance degradation. As a result, photodegradation efficiency lowers as MB concentration increases.

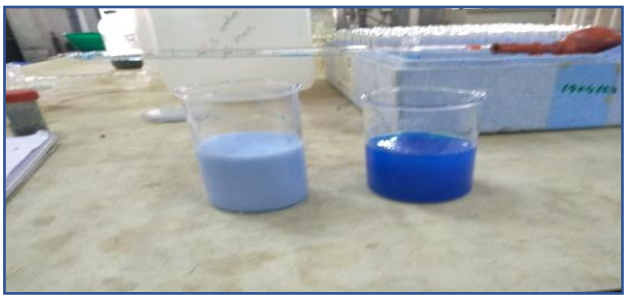


Figure 1 Color removal of Methylene Blue

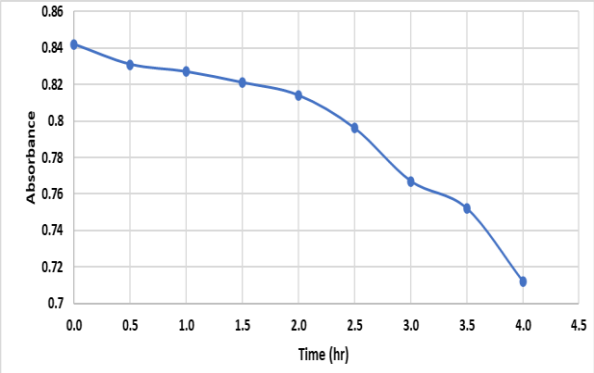


Figure 2 Absorbance of 0.01ppm Methylene Blue vs exposure time

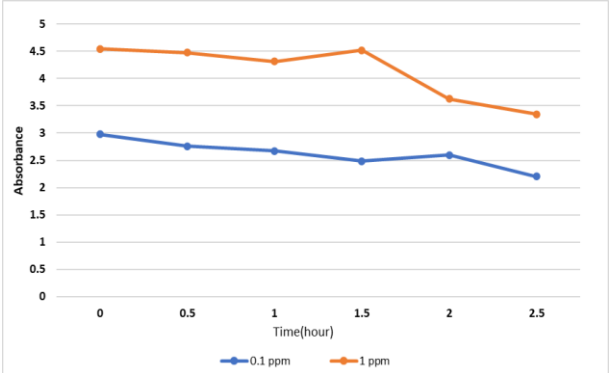


Figure 3 Absorbance of 0.1ppm and 1ppm MB with exposure time

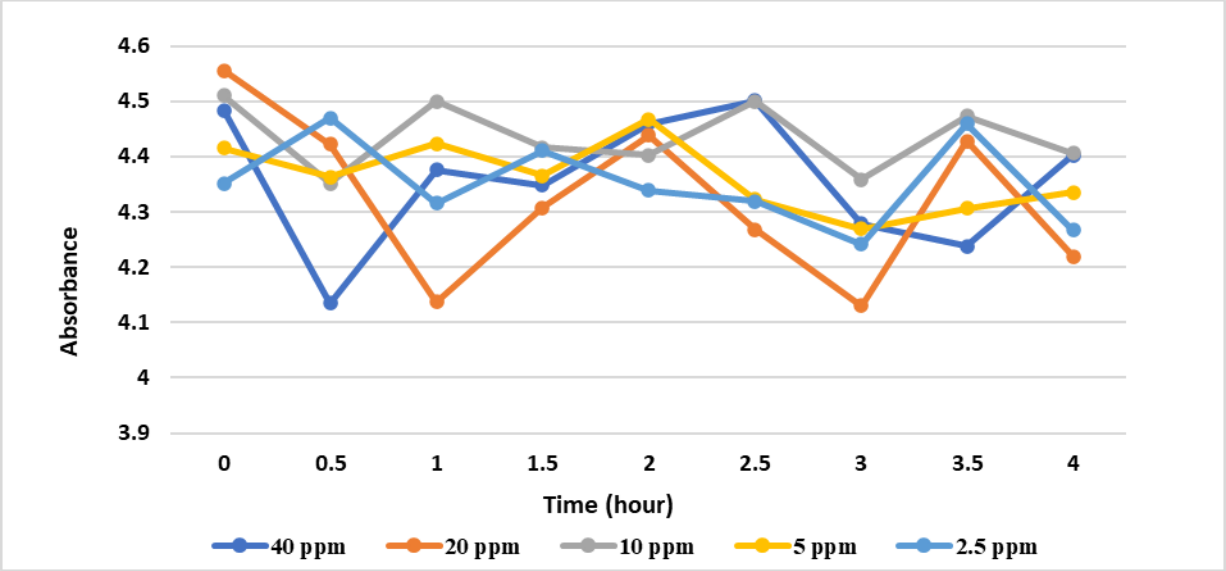


Figure 4 Absorbance of unfiltered MB concentrations (ppm) with exposure time

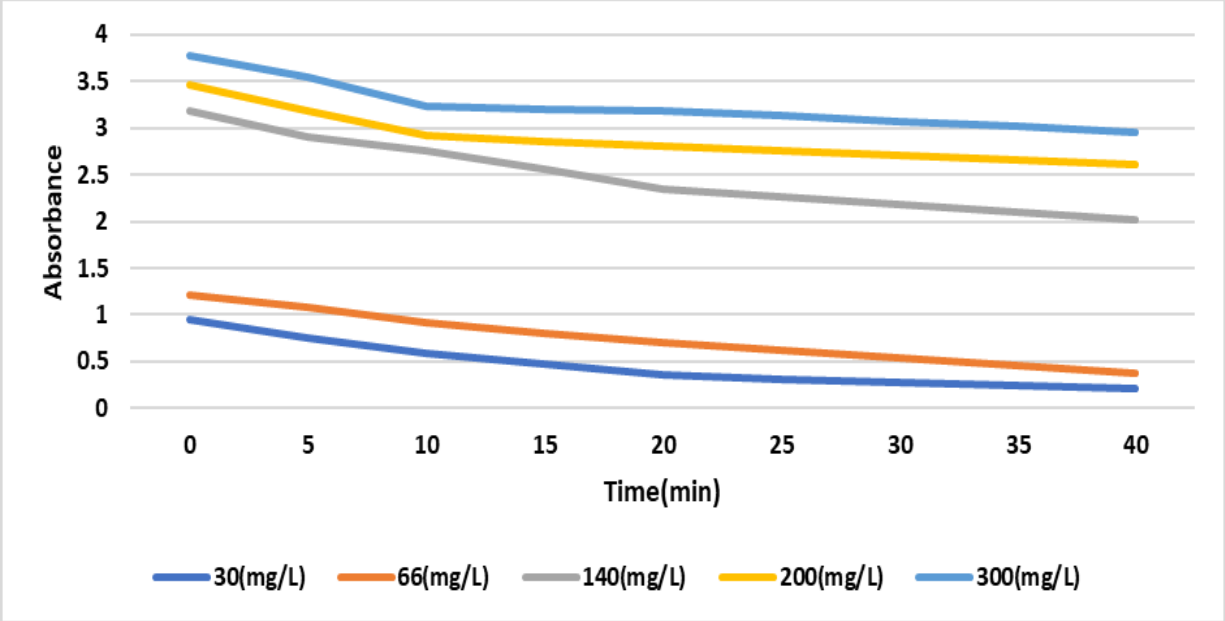


Figure 5 Absorbance of filtered MB concentrations (ppm) with exposure time

3.2 Color Removal of Tannery wastewater

Two samples of tannery wastewater were taken to observe color and EC (Electrical Conductivity) for different exposure times. Sample-1 was kept in the UV chamber for lower exposure time (10 minutes and 20 minutes). Sample-2 was kept in the UV chamber for higher exposure time (30 minutes and 50 minutes). The absorbance of tannery wastewater was obtained using a UV-vis spectrophotometer at a 664nm spectrum wavelength. The color and electrical conductivity of tannery wastewater reduce as the exposure time in the UV chamber increases. The color reduction rate was 27% and the EC reduction was 26% for sample-1. The reduction trend is shown in figures 6 and 7. The EC reduction was about 13% and color removal was 51% for sample-2 and the decreasing trend is shown in figures 8 and 9. The actual color of Tannery wastewater was measured by filtering it two times to remove suspended solids. Electrical conductivity was also measured, along with the color of the wastewater. In this experiment, the concentration of TiO_2 was 0.5 g/L. The color of wastewater degrades with the increase in exposure time under UV light. The visual representation of the color reduction of tannery wastewater is shown in figure 10.

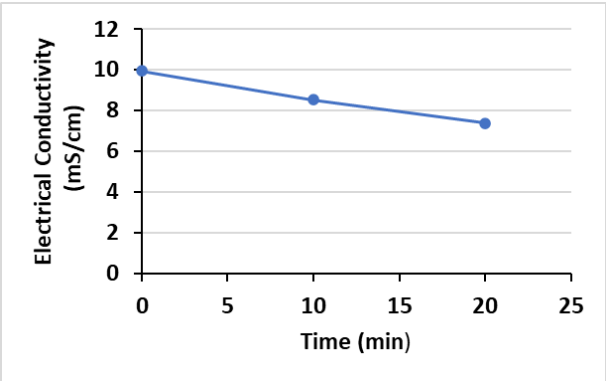


Figure 6 EC reduction of tannery wastewater (sample-1)

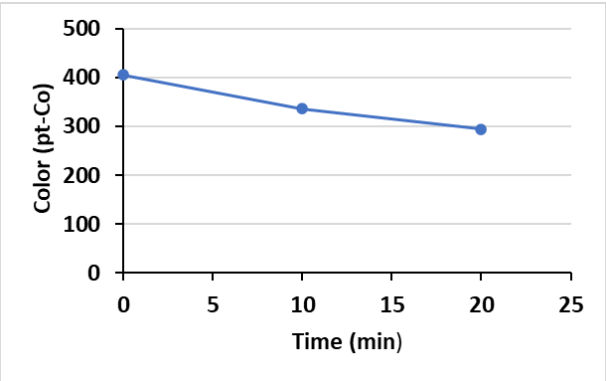


Figure 7 Color degradation of tannery wastewater (sample-1)

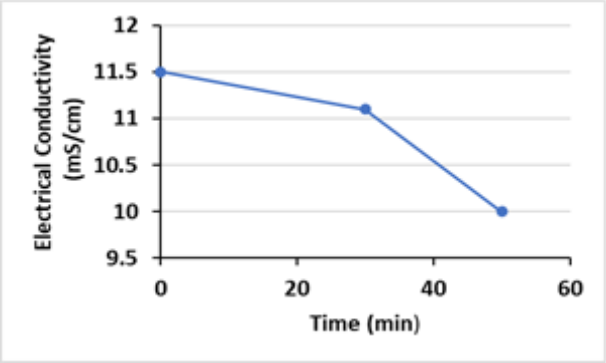


Figure 8 Color degradation of tannery wastewater (sample-2)

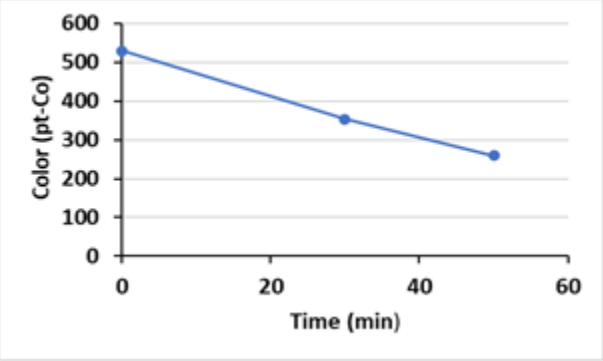


Figure 9 EC reduction of tannery wastewater (sample-2)

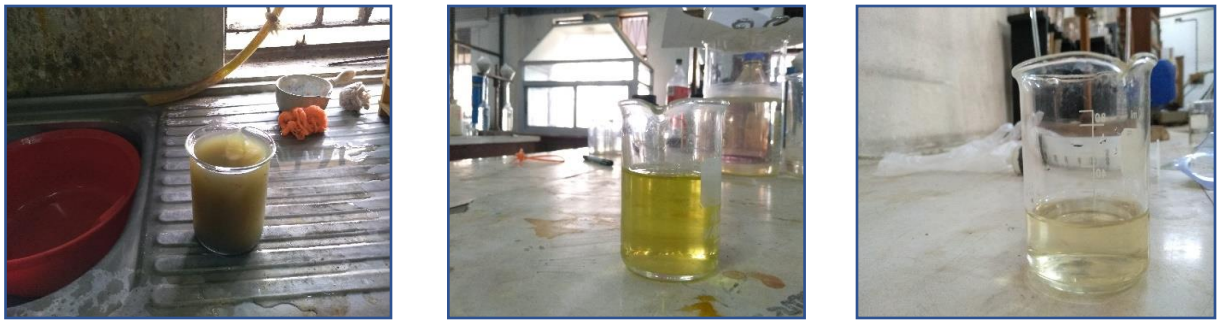


Figure 10 Color reduction of tannery wastewater

4.0 CONCLUSION AND RECOMMENDATIONS

This study has two parts. Firstly, photodegradation was done for MB and secondly, this concept was used to remove the color of tannery waste water. The main findings of this study are: Without filtering, absorbance reduction was very low. Absorbance of 0.1 ppm and 1.0 ppm Methylene Blue was compared. In both cases, absorbance decreasing rate was slow as the final solution was not filtered. Filtering the MB solution after UV light exposure improves photo degradation significantly as the presence of suspended particles causes interference in absorbance reading. Absorbance reduction of a low concentrated MB solution was more satisfactory than the higher concentration. The absorbance of a higher concentration of Methylene Blue showed scattered values. Electrical conductivity and pH were also measured, along with the color of the wastewater. The pH value remained constant through the whole experiment but the EC was reduced slightly. The color removal efficiency of TiO_2 for tannery waste water was moderate. The author recommends that, for better results,

- Different percentages of carbon and nitrogen can be examined for doping of TiO_2 to get a better result.
- Preparation of co-doped TiO_2 can be more accurate.
- Absorbance can be measured immediately after exposure of UV light. During this study, the distance between the UV chamber and UV-vis spectrophotometer was about 120m. As a result, absorbance could not be measured immediately.
- Other parameters can be measured.

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References

[1] Cong, Y., Chen, F., Zhang, J., & Anpo, M. 2006. Carbon and nitrogen-codoped TiO_2 with high visible light photocatalytic activity. *Chemistry Letters, 35*(7): 800-801.

[2] Fujishima, A., Rao, T. N. and Tryk, D. A. 2000. Titanium dioxide photocatalysis. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews, 1*(1): 1–21. doi:10.1016/s1389-5567(00)00002-2.

[3] Hasan, M. M., Haseeb, A. S. M. A., Saidur, R., & Masjuki, H. H. 2008. Effects of annealing treatment on optical properties of anatase TiO_2 thin films. *International Journal of Chemical and Biological Engineering, 1*(2): 92-96.

[4] Hou, C., Hu, B. and Zhu, J. 2018. Photocatalytic degradation of methylene blue over TiO_2 pretreated with varying concentrations of NaOH. *Catalysts, 8*(12): 575. doi:10.3390/catal8120575.

[5] Li, J., Ma, W., Chen, C., Zhao, J., Zhu, H. and Gao, X. 2007. Photodegradation of dye pollutants on one-dimensional TiO_2 nanoparticles under UV and visible irradiation. *Journal of Molecular Catalysis A: Chemical, 261*(1): 131–138. doi:10.1016/j.molcata.2006.08.018.

[6] Paul, H., Antunes, P., Covington, A. D., Evans, P. and Phillips, P.S. 2013. Bangladeshi leather industry: An overview of recent sustainable developments. *Journal of the Society of Leather Technologists and Chemists*. *97*(1): 25-32.

[7] Schneider, J., Matsuoka, M., Takeuchi, M., Zhang, J., Horiuchi, Y., Anpo, M. and Bahnemann, D. W. 2014. Understanding TiO_2 photocatalysis: Mechanisms and materials. *Chemical Reviews, 114*(19): 9919–9986.doi:10.1021/cr5001892.

[8] Song, L. Y., Wu, Y. C. and Lu, X. F. 2007. Preparation and characterization of doped nanometer TiO_2. *Advanced Materials Research, 26-28*: 649–652. doi:10.4028/www.scientific.net/amr.26-28.649.

[9] Tayade, R. J., Natarajan, T. S. and Bajaj, H. C. 2009. Photocatalytic degradation of Methylene Blue dye using ultraviolet light emitting diodes. *Industrial & Engineering Chemistry Research, 48*(23): 10262–10267. doi:10.1021/ie9012437.

[10] Thiruvenkatachari, R., Kwon, T. O., Jun, J. C., Balaji, S., Matheswaran, M. and Moon, I. S. 2007. Application of several advanced oxidation processes for the destruction of terephthalic acid (TPA). *Journal of Hazardous Materials, 142*(1-2): 308–314. doi:10.1016/j.jhazmat.2006.08.023

[11] Valdés, Á. and Kroes, G.-J. 2010. Cluster study of the photo-oxidation of water on rutile titanium dioxide (TiO_2). *The Journal of Physical Chemistry C, 114*(3): 1701–1708. doi:10.1021/jp909606r.

[12] Xu, C., Rangaiah, G. P. and Zhao, X. S. 2014. Photocatalytic degradation of Methylene Blue by titanium dioxide: Experimental and modeling study. *Industrial & Engineering Chemistry Research, 53*(38): 14641–14649. doi:10.1021/ie502367x.

[13] Yu, J. C., Yu, J., Ho, W., Jiang, Z. and Zhang, L. 2002. Effects of F-doping on the photocatalytic activity and microstructures of nanocrystalline TiO_2 powders. *Chemistry of Materials, 14*(9): 3808–3816.doi:10.1021/cm020027c.

[14] Zaleska, A. 2008. Doped-TiO_2: A review. *Recent Patents on Engineering, 2*(3): 157–164. doi:10.2174/187221208786306289