

Photochemical treatment of blue-indigo using TiO₂-sunlight system in heterogeneous conditions.[†]

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Abstract: Ecuador is one of the countries in the Latin American region with high textile production. However, chemical treatment strategies in the Ambato, Tungurahua and Quito areas are inefficient and not systematically applied, and the volumes of dyes and pigment-type contaminants generate serious environmental problems. The treatments of indigo textile wastewater and related indigo derivatives are very complex. Taking these into consideration, was developed a simple photochemical protocol, in heterogeneous conditions, for degrading “blue-indigo” (Ambato textile group) in solution, using TiO₂ (Degussa P25, with purity of ≈ 99 % and BET surface area 50 ± 15 m²/g) and solar light at lab scale. The photocatalytic oxidation of “blue indigo” in aqueous solution was assessed by solar irradiation, in the presence of TiO₂ particles. The effect of indigo concentrations, pH and TiO₂ loading for maximum degree of degradation were evaluated. The mineralization of “blue indigo” was reported by measuring COD-i and COD-f of the solution that was irradiated with sun light under optimized conditions. The results allows to re-design, in eco-sustainable conditions, for Ecuador, the strategies for controlling contamination in textile wastewaters.

Keywords: Photocatalysis; textile industrial effluents; titanium dioxide; sunlight.

1. Introduction

Ecuador is one of the countries in the Latin American region with high textile production. However, chemical treatment strategies in the Ambato, Tungurahua, Esmeraldas and Quito areas are inefficient and not systematically applied, and the volumes of organic dyes and pigment-type contaminants generate serious environmental problems, considering their ecological toxicity, carcinogenicity and high resistance to biodegradation. Several physico-chemical and biotechnological methods have been reported in the past 10 years but these processes have high operating cost and are of limited applicability in eco-sustainable conditions. Photo-catalytic oxidative degradation using solar light is the preferred alternative procedure to clean-up polluted waters due to its simplicity, functionality, potential scalability and cost effectiveness at laboratory or meso-scale in micro-textile entrepreneurship [1, 2]. Various types of photo-catalysts such as perovskites, titanates, metal oxides, niobates, nanomaterials composites and semiconductors have been

extensively used. TiO₂ has been proved to be an excellent catalyst in the oxidative photo-degradation of organic pollutants.

The use of high-energy UV light is not only operationally expensive, it is instrumentally demanding but it can also generate serious hazard problems. Therefore, the use of visible light, sunlight, constitutes an interesting variant for treating textile wastewater in ecologically friendly conditions. It has been demonstrated how the photo-bleaching (partial oxidative degradation) of dyes could be achieved by sunlight irradiation using TiO₂ as photo-catalyst [3,4]. Taking into consideration that no much information have been reported on photocatalytic oxidative degradation of blue indigo by TiO₂ (anatasa)/sunlight system, and its advantage at micro- and meso technological scale, the main objective of the report is evaluate the capability of proposed system (vide supra) to decolorize and degrade residual aqueous solution of indigoid dye blue indigo using solar light with commercial TiO₂ photo-catalyst.

2. Materials and Methods

The TiO₂/visible light (sunlight) photo-catalysis experiments were carried out in the facilities of the Chemical Technology laboratories of the Chemical Engineering Campus at Technical University of Esmeraldas "Luis Vargas Torres, Esmeraldas, Ecuador, (0° 58'25"; N 79° 39'59" W). TiO₂ used in the experiment was Degussa P-25 (QUIMPAC supplier-Ecuador, 90% anatase) with an average particle size of 30 nm and surface area of 50 m²/g and was used as provided by national supplier. The organic dye "blue indigo" was obtained from textile industry REALTEC S.A., Esmeraldas, Ecuador, and was used without any purification. The sample of residual water with blue indigo was supplied by REALTEC S.A, Ecuador. (Figure 1 a, b)

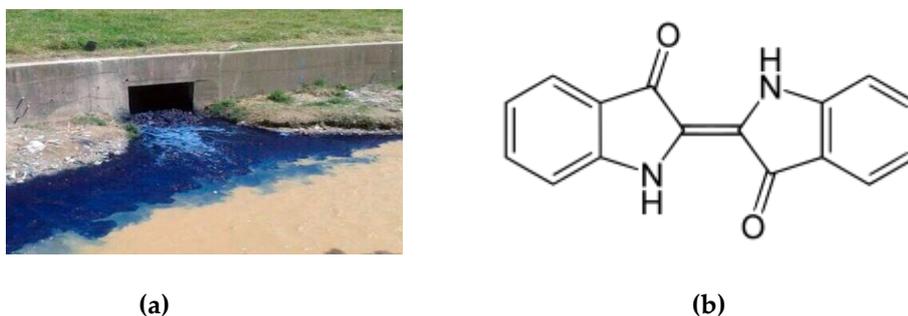


Figure 1. a) Textile residual water from REALTEC S.A, Esmeraldas, Ecuador, 20th June 2020 photo by the authors EFMQ; b) molecular structure of "blue indigo".

The photochemical reactor (cylindrical configuration) of 500 ml capacity was made-up of borosilicate glass having dimensions 18 cm x 10 cm (height x diameter) with a port at the top for sampling. Solar light was used as the energy source for catalyst activation and assess field efficiency. Experiments were performed at ambient temperature. The reactor assembly was placed on a magnetic stirring plate to further enhance the agitation avoiding sedimentation of the catalyst. The slurry composed of the dye residual solution from REALTEC S.A. and catalyst (TiO₂, 1000 mg) placed in the reactor was directly exposed to natural solar light for specified time interval. A centrifuge (QUIMPAC-Ecuador,), operated at 3600 rpm, was utilized for removing the TiO₂ and to obtain the supernatant for UV/VIS (Hitachi U-2001 spectrophotometer, Japan) determination, in the range of $\lambda = 400-700$ nm. The percentage of degradation was calculated by measuring changes in absorbance and COD. Chemical oxygen demand (COD) was measured by the closed reflux method [JAPHA, 1989]

3. Results and Discussion

Time taken for maximum degradation of the waste dye solution was around 80-110 minutes of irradiation. Beyond 100 minutes, the degradation was found to be negligible (Figure 2). From the

results obtained it can be concluded that the photo-catalytic approach promotes the decline of chromophore peaks in the dye molecule in 80-100 minutes. In this case, the chemical oxygen demand was used as an indicative parameter of the photo-oxidative degradation process of indigo blue at a dose of 1000mg of the photo-catalyst.

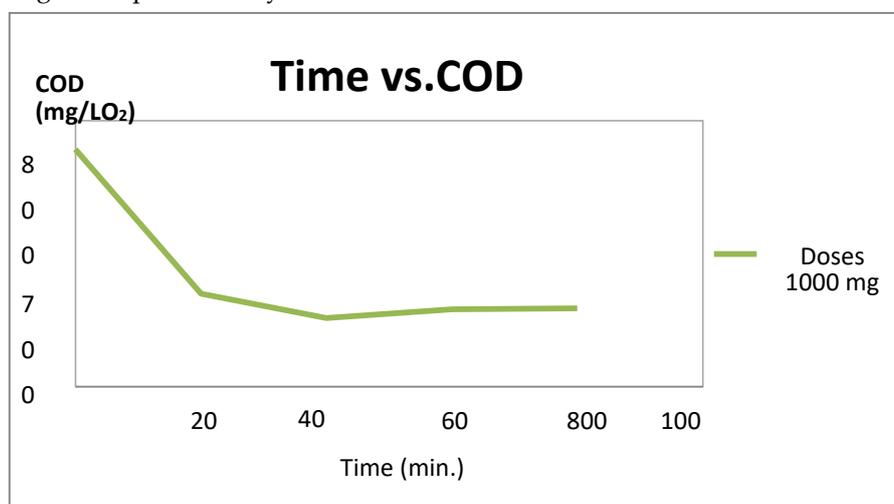


Figure 2. Chemical Oxygen Demand (COD) vs. Time and TiO₂ doses at 1000 mg

The results of average removal percentages of Apparent Color (AP) for 1000 mg of Titanium Dioxide at the different residence times are shown in the Table 1 and Figure 3.

Time of residence (min)	Average AP	% Average Removal
20	0,393	72,58
40	0,390	72,78
60	0,393	72,58
80	0,399	72,18

Table 1. % Average Removal of blue indigo color vs. residence time of TiO₂ in the photoreactor.

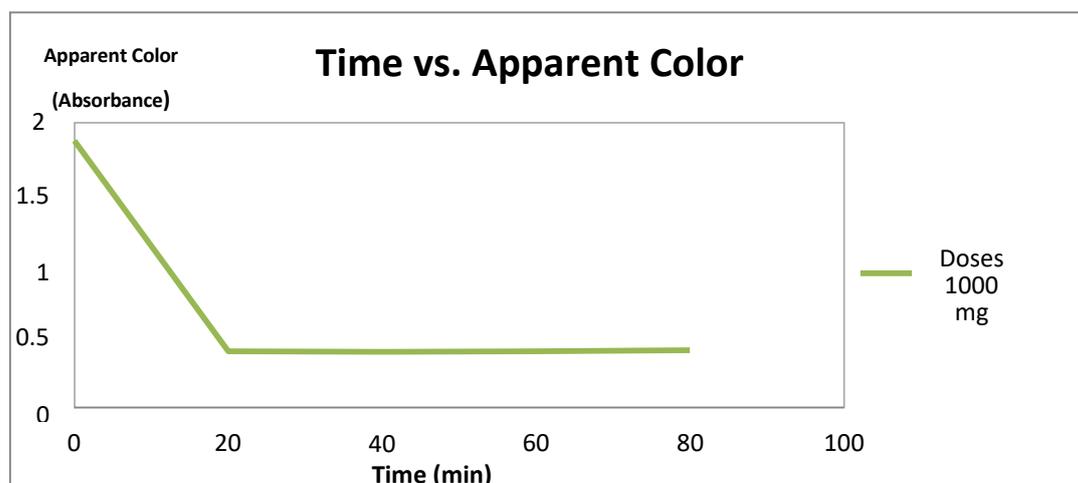
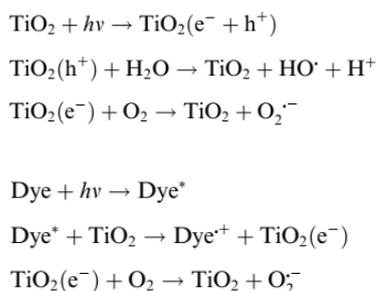


Figure 3. Variations of Apparent Color vs. Time and TiO₂ doses at 1000 mg.

A blank experiment in the absence of solar irradiation (2h) illustrated the adsorption equilibrium of the waste dye solution onto TiO₂. Another experiment of solar irradiation (2h) of the dye solution in the absence of TiO₂ showed no significant photo-oxidative degradation of the waste slurry, indicating that this phenomenon is photo-catalytic in nature.

The mechanism for photo-oxidative degradation (bleaching) in correspondence with a historical perspective could proceed as follows [5]:



This photosensitizing oxidation mechanism suggests that the electron from the excited dye molecule is transferred into the conduction band of the TiO₂, and the cation radical formed at the surface of TiO₂ quickly undergoes photo-degradation to intermediate products as depicted in Figure 4 [5,6].

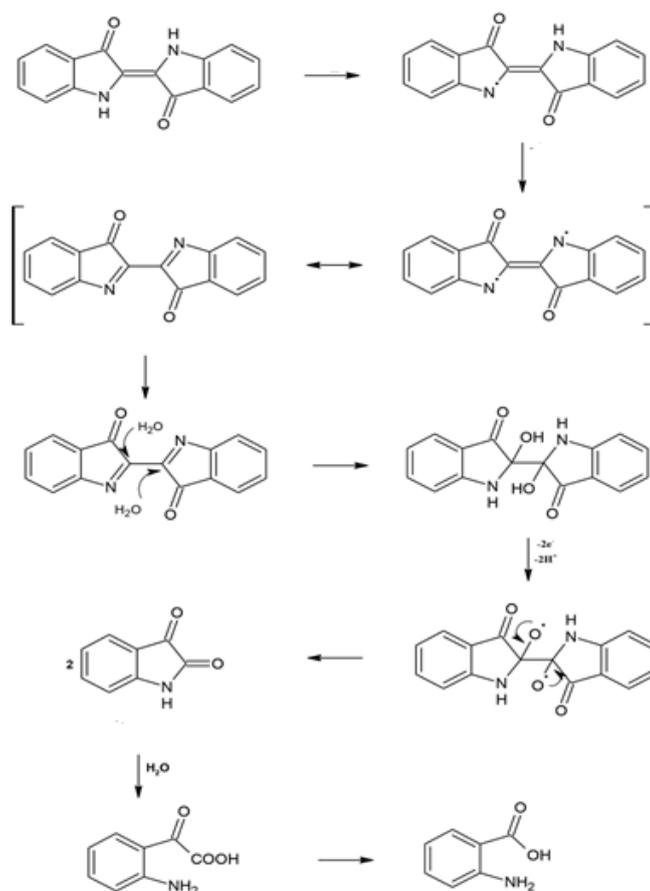


Figure 4. Probable mechanism of initial photo-oxidative degradation of blue indigo under TiO₂/sunlight system and mechanical stirring

4. Conclusions

A TiO₂/sunlight system was developed to photo-oxidative degradation of an organic dye “blue indigo”. Natural sunlight can be used for oxidative photo-degradation of this indigoid pigment particularly rapidly under these very simply and eco-sustainable conditions. Blue indigo was degraded in the presence of TiO₂ photo-catalyst in the form of suspension by irradiation with solar light. Hence the photo-oxidative degradation of textile dyes of indigoid nature employing solar energy may emerge as a viable method because of its eco-sustainability, cost effective and technological simplicity.

Author Contributions: EFMQ participated in the conceptualization and investigation at laboratory scale of the article on the basis of his master degree thesis; JETM participated in the methodology, investigation and original draft preparation, review and editing; GCM contributed with formal analysis, experimental data validation and project administration.

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Conflicts of Interest: The authors declare no conflict of interest.

References

1. Alahiane, S. Qourzal, M. El Ouardi, M. Belmouden, A. Assabbane, Y. Ait-Ichou, Adsorption and photocatalytic degradation of indigo carmine dye in aqueous solutions using TiO₂/UV/O₂, *J. Mater. Environ. Sci.* **4** (2013) 239.
2. Rauf, M. A., & Ashraf, S. S. Fundamental principles and application of heterogeneous photocatalytic degradation of dyes in solution. *Chemical Engineering Journal*, (2009) 151(1-3), 10–18.
3. Mondal K, Sharma A. Photocatalytic Oxidation of Pollutant Dyes in Wastewater by TiO₂ and ZnO nano-materials – A Mini-review. *The National Academy of Sciences India (NASI)*: (2014), 36–72.
4. Jawad A., Nur Shazwani, Mohd I., Ismail K. & Nawawi W. Kinetics of photocatalytic decolourization of cationic dye using porous TiO₂ film, *Journal of Taibah University for Science*, (2016) 10:3, 352-362.
5. Bahrudin, N.N., Nawi, M.A. & Nawawi, W.I. Enhanced photocatalytic decolorization of methyl orange dye and its mineralization pathway by immobilized TiO₂/polyaniline. *Res. Chem. Intermed.* (2019) 45, 2771–2795.
6. Zhang, F., Zhao, J., Zang, L., Shen, T., Hidaka, H., Pelizzetti, E., Serpone, N. Photoassisted degradation of aqueous surfactant/TiO₂ dispersion under visible light irradiation. *J. Chem. Soc., Faraday Trans.* (1997) 94, 673–676.

