



PHOTOLYTIC REDUCTION OF METHYLENE BLUE BY SnO₂ NANOPARTICLES

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Abstract : This study has been undertaken to investigate the photocatalytic activities such as degradation rate, time required to complete the degradation and kinetics of azo class of Methylene Blue (MB) dye by using SnO₂ Metal Oxide Nano (MONP) Particles as a catalyst.

Keywords – Methylene Blue, Benzophenone, SnO₂, Aloe vera, Acalypha indica

1. INTRODUCTION

1.1 Photo reduction by sunlight in presence of benzophenone.

Alpha – hydroxyl ketones and their derivatives are extensively used in the photo curing of coating. The photochemistry is well investigated and some unsubstituted derivatives are biodegradable [1-5]. These compounds produce highly reactive free radicals on exposure to natural sunlight that is without the need for high power lamps often used in other photo degradation methods. In this investigation, benzophenone is employed as they are biodegradable and hence after aerobic biodegradation would not add to final carbon load in the water and therefore it was chosen as reducing generated on photolysis as the carbon centered free radicals generated on photolysis are reducing in nature [6-10].

2 Experimental works: Photolytic Degradation of MB by SnO₂ NPs

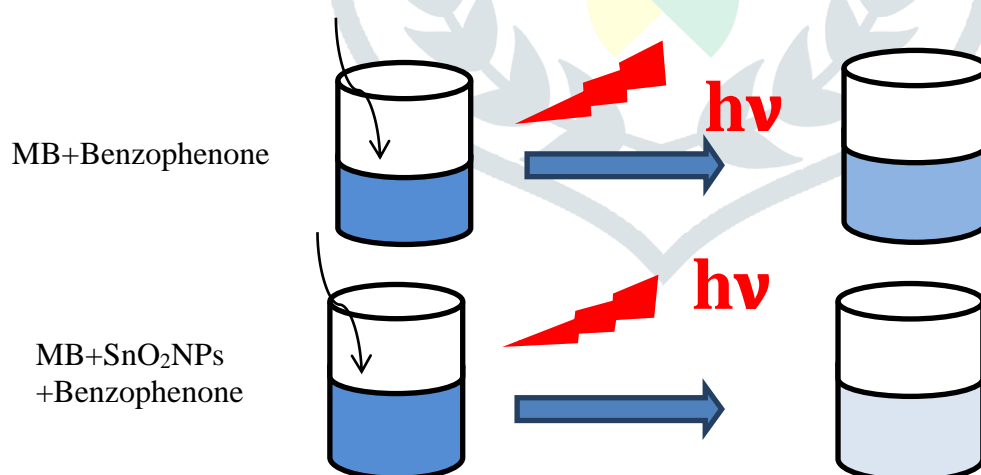
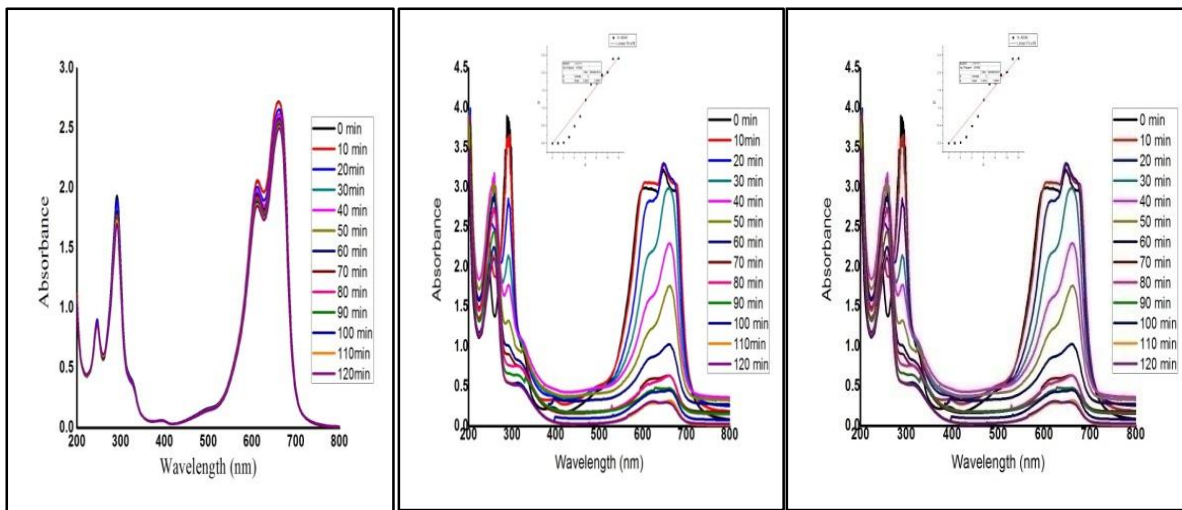


Fig. 1: Photolytic Degradation of MB by SnO₂ NPs

Methylene Blue was prepared by crushing the Methylene Blue dye in a mortar in crude ethanol. Similarly benzophenone was prepared in crude ethanol[11-14]. A reaction mixture containing 4ml of 10⁻⁴ M Methylene Blue and 0.150ml of 0.05 M benzophenone in a total volume of 50 ml was exposed to sunlight by adding distilled water [16,19]. The absorbance of Methylene blue was monitored at 520 nm as a function of time. Similar reaction mixture of 50 ml in addition of 1ml of SnO₂ NPs with different protecting materials was exposed to sunlight and the absorbance was monitored at 520 nm.

4.4.5 Analysis of Photolytic Degradation of Methylene Blue by SnO₂ NPs

a) Photolytic Degradation of MB Without NPs

b) Photolytic Degradation of MB by SnO₂ NPs using Aloe verac) Photolytic Degradation of MB by SnO₂ NPs using Acalypha indicaFigure 2: Analysis of Photolytic Degradation of MB by SnO₂ NPs

The Photolytic degradation of MB in attendance of SnO₂ NPs showed a maximum absorption band (λ_{max}) at 667 nm with a shoulder at 610 nm [19] whereas, the strong absorptions also located at 292 nm and 246 nm in UV-Vis spectrum. The λ_{max} at 664 nm was due to of the absorption of cyclic imine group, 292 nm was due to the absorption of poly cyclic earrings present in MB and 246 nm was due to absorption of the formed amino group [2-5]. This catalytic reaction can be simply escorted UV-Vis spectrophotometrically because the λ_{max} of MB is well separated from the surface Plasmon absorption of SnO₂ NPs.

In the absence of SnO₂ NPs as a catalyst, the photolytic degradation of MB via sunlight become extremely sluggish this is shown in Figure 2 (a). It was discovered that the intensity of λ_{max} at 667 nm stays almost unaffected for several hours when a blank experiment was performed without SnO₂ NPs as a catalyst [15-17]. Hence, this reaction was not kinetically favorable in the absence of SnO₂ NPs and couldn't be recognized only in presence of sunlight. But the degradation of MB started out instantly upon the addition of SnO₂ NPs as a catalyst. This was noticeable from the fading of the blue color of the reaction medium in addition to the lower in depth of the peak at 667 nm [17]. The reaction was completed in 120 min which was evident from almost zero absorption at 667 nm shows in figure 2 (b-c). Thus, the photolytic degradation of MB in the absence of the SnO₂ NPs was thermodynamically favorable but not kinetically. SnO₂ NPs catalyst supplied an alternative path of low activation energy for the photolytic degradation of MB which reduced the kinetic barrier thereby making it thermodynamically in addition to kinetically favorable [18].

5.4.6 Kinetics studies for photolytic degradation of MB by SnO₂NPs

The kinetics study for the photolytic deprivation of MB catalyzed by SnO₂ NPs in attendance of sunlight was carried out by using the Langmuir-Hinshelwood mechanism [17 -18].

Rate constant k is the pseudo first order velocity constant, decided from the Langmuir-Hinshelwood expression given by using following equation

$$\ln \frac{C_0}{C_t} = Kt$$

Where C_0 and C_t are the initial and very last concentrations having equal in terms of A_0 and A_t correspondingly and tested at a fixed wavelength at time t , a plot of $\ln (A_0/A_t)$ with time offers a straight line whose slope is the k . Hence, k is the pseudo first order rate constant for SnO₂ NPs.

The reaction rate constant is found to be as below given table

Photolytic degradation of MB in presence of	Reaction rate constant
Without NPs	0.000001 min ⁻¹
SnO ₂ NPs. (Using Aloe vera)	0.018 min ⁻¹
SnO ₂ NPs. (Using Acalypha indica)	0.012 min ⁻¹

Table 1: Analysis of Photolytic Degradation of MB by SnO₂ NPs

5.5 Conclusions

The following broad conclusions may be drawn:

- Kinetics of degradation of MB has been investigated and found to be pseudo first order. The Rate Constant for degradation of MB it is 0.018 min⁻¹ for aloe vera and 0.012 min⁻¹ for acalypha indica.

References

- 1) Dnyaneshwar R. Shinde, Popat S. Tambade, Manohar G. Chaskar, and Kisan M. Gadave (2017) Photocatalytic degradation of dyes in water by analytical reagent grades ZnO, TiO₂ and SnO₂: a comparative study 16 November 2017 <https://doi.org/10.5194/dwes-10-109-2017>
- 2) Archita Bhattacharjee, M. Ahmaruzzaman, A green approach for the synthesis of SnO₂ nanoparticles and its application in the reduction of p- nitro phenol Materials Letters <http://dx.doi.org/10.1016/j.matlet.2015.05.053> 0167-577X/& 2015 (M. Ahmaruzzaman). Materials Letters 157 (2015)260–264
- 3) Lalitha Gnanasekaran, R. Hemamalini, R. Saravanan, K. Ravichandran, F. Gracia, Shilpi Agarwal, Vinod Kumar Gupta, Science Direct Journal of Photochemistry & Photobiology, B: Biology Synthesis and characterization of metal oxides (CeO₂, CuO, NiO, Mn₃O₄, SnO₂ and ZnO) nanoparticles as photo catalysts for degradation of textile dyes
- 4) Muthu GnanaTerasa Nathan, P. Myvizhi, Green Synthesis and Characterization of Tin Oxide Nanoparticles Using Plant Extract International Journal of Pure and Applied Mathematics Volume 119 No. 12 2018, 6439-6448 ISSN: 1314-3395 (on-line version)
- 5) Rida Javed, Faisal Nawaz, Muhammad Sohail, Iqba Ahmad, Fabrication of SnO₂/CQDs composite for photocatalytic degradation of malachite green dye. Journal of Contemporary Research in Chemistry (2016) 1(1): 42-50
- 6) A. Ghaderi, S. Abbasi, F. Farahbod Research note Synthesis of SnO₂ and ZnO Nanoparticles and SnO₂-ZnO Hybrid for the Photocatalytic Oxidation of Methyl Orange, Iranian Journal of Chemical Engineering Vol. 12, No. 3 (Summer 2015), IACHE
- 7) Nasir, Z., Shakir, M., Wahab, R., Shoeb, M., Alam, P., Khan, R. H., & Mobin, M. (2017). Co-precipitation synthesis and characterization of Co doped SnO₂ NPs, HSA interaction via various spectroscopic techniques and their antimicrobial and photocatalytic activities. International journal of biological Macromolecules, 94, 554-565.
- 8) Junjie Hu, Biosynthesis of SnO₂ Nanoparticles by Fig (Ficus Carica) Leaf Extract for Electrochemically Determining Hg(II) in Water Samples, International Journal of Electrochemical Science, 10 (2015) 10668 - 10676
- 9) J. Gajendran and V. Rajendran, Synthesis and Characterization of Ultrafine SnO₂ Nanoparticles via Solvo thermal Process, International Journal of Physics and Applications. ISSN 0974-3103 Volume 2, Number 1 (2010), pp. 45—50
- 10) Viet, P. V., Thi, C. M., & Hieu, L. V. (2016). The high photocatalytic activity of SnO₂ nanoparticles synthesized by hydrothermal method. *Journal of Nanomaterials*, 2016.
- 11) L. Fua, B. Y. Zhenga, Q. Rena, A. Wangc, B. Dengd, Green Biosynthesis Of SnO₂ Nanoparticles By Plecranthus Amboinicus Leaf Extract Their Photocatalytic Activity Toward Rhodamine B Degradation
- 12) Senthilkumar S, Rajendran A (2017) Eco-friendly Synthesis and Characterization of Nanostructure SnO₂ Thin Films Using Citrus aurantifolia Peel Extract by Spin Coating Method. J Nanomed Res 6(4): 00164. DOI: 10.15406/jnmr.2017.06.00164 Journal of Ovonic Research Vol. 11, No. 1, January - February 2015, p. 21 - 26

- 13) Koli Prashant B. and Kapadnis Kailas H, Green synthesis and characterization of SnO₂ and ZnO nanoparticles: Study their electrical conductivity and gas sensing properties, Der ChemicaSinica, 2016, 7(2): 29-35 ISSN: 0976-8505. Iranian Journal of Chemical Engineering Vol. 12, No. 3 (Summer 2015), IACHe
- 14) Soma Gorai, Gorai et al., J. Mater. Environ. Sci., 2018, Volume 9, Issue 10, Page 2894-2903 Bio-based Synthesis and Applications of SnO₂ Nanoparticles - An Overview
- 15) SethumadhavanSudhaparimala, Arumugam Gnanamani A., Asit Baran Mandal. Green Synthesis of Tin Based Nano Medicine: Assessment of Microstructure and Surface Property. American Journal of Nanoscience and Nanotechnology. Vol. 2, No. 4, 2014, pp. 75-83. doi: 10.11648/j.nano.20140204.13
- 16) Ahmed, A., Siddique, M. N., Alam, U., Ali, T., & Tripathi, P. (2019). Improved photocatalytic activity of Sr doped SnO₂ nanoparticles: a role of oxygen vacancy. *Applied Surface Science*, 463, 976-985.
- 17) Annamalai Rajendran, Eco-friendly Synthesis and Characterization of Nanostructure SnO₂Thin Films Using Citrus aurantifolia Peel Extract by Spin Coating Method Volume 6 Issue 4 - 2017, J Nanomed Res 2017, 6(4): 00164
- 18) L. Fua,B, Y. Zhenga, Q. Rena, A. Wangc, B. Deng, Green Biosynthesis Of SnO₂ Nanoparticles By PlectranthusAmboinicus Leaf Extract Their Photocatalytic Activity Toward Rhodamine B Degradation
- 19) Farhadi, A., Mohammadi, M. R., & Ghorbani, M. (2017). On the assessment of photocatalytic activity and charge carrier mechanism of TiO₂@ SnO₂ core-shell nanoparticles for water decontamination. *Journal of Photochemistry and Photobiology A: Chemistry*, 338, 171-177

