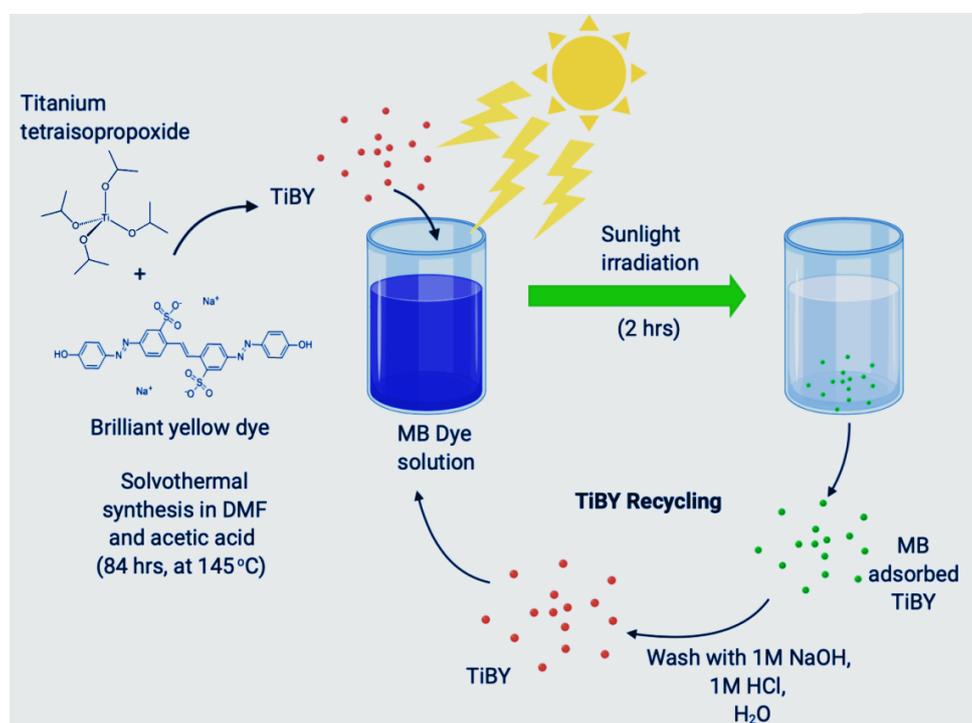


Dual functioning TiO₂-brilliant yellow composite for efficient removal of methylene blue from water

I.R. Perera*, Y. Wijesundara and C.V. Hettiarachchi



Highlights

- TiO₂/dye composite was synthesized using one pot solvothermal technique.
- The composite showed a dual functionality as an adsorbent and a photocatalyst.
- High dye removal efficiency (97% in 2 h without H₂O₂) was achieved for methylene blue dye.
- A remarkable reusability was observed even after three cycles of use.

RESEARCH ARTICLE

Dual functioning TiO₂-brilliant yellow composite for efficient removal of methylene blue from water

I.R. Perera*, Y. Wijesundara and C.V. Hettiarachchi

Department of Chemistry, Faculty of Science, University of Peradeniya, Peradeniya 20400, Sri Lanka.

Received: 30/09/2020; Accepted: 04/05/2021

Abstract: A novel composite of titanium dioxide and brilliant yellow dye (Ti-BY) was synthesized using one-pot synthesis technique under solvothermal conditions. The composite was stable in both acidic and basic conditions and also Ti-BY demonstrated dual functionality in the removal of methylene blue dye from water, in which it was found to be active as a photocatalyst as well as an adsorbent. Remarkably, the composite was 56% efficient in the dark and 97% under sunlight irradiation within 2 h at pH 11 without H₂O₂.

Keywords: Photocatalysis; adsorption; titanium dioxide; brilliant yellow; methylene blue.

INTRODUCTION

Water pollution is one of the main environmental crises that we face today as it limits the consumable volume of water, space available for aquatic systems and increase health risks in living beings. One significant method of water pollution occurs due to the release of untreated synthetic dyes from industries such as paper production, leather tanning, food and textile (Lellis *et al.*, 2019; Yaseen and Scholz, 2019). The degradation products of these dyes are toxic or even carcinogenic to human and aquatic life and also increase the toxicity and chemical oxygen demand (COD) and biological oxygen demand (BOD) levels of aquatic sources (Crini, 2006; Lellis *et al.*, 2019). In order to remove these dyes from effluents many physicochemical methods such as filtration, flocculation, electrocoagulation, photocatalytic degradation and adsorption have been investigated (Sharma *et al.*, 2018; Jamee and Siddique, 2019; Shindhal *et al.*, 2021). Photocatalytic degradation is one of the preferred techniques used due to the ability of degrading toxic materials into non-toxic and environment friendly compounds. Biomass degradation (Al Zoubi *et al.*, 2021; Hussain *et al.*, 2021; Sriramoju *et al.*, 2021) Fenton process (Babuponnusami and Muthukumar, 2014), degradation by semiconductors such as TiO₂, ZnO and their derivatives (Miranda-García *et al.*, 2011) are few of the commonly utilized methods of catalytic degradation (Forgacs *et al.*, 2004). However, degradation of some of the synthetic dyes is challenging due to their high stability under light and oxidation processes (Sing, 1998). Adsorption technique is widely practiced for removal of dyes which are resistant for degradation and due to its

high efficiency, comparatively low cost, reusability and facile regeneration of the adsorbent (K. Ramakrishnan *et al.*, 2021; Yu *et al.*, 2021). Porous materials such as alginate beads, activated carbons, zeolites, metal organic frameworks, polymeric resins, metal matrix composites and clays are some of the examples for materials used in adsorptive removal (Haque *et al.*, 2011). Recently, we reported a one-pot synthesis technique to impregnate a high amount of N719 dye on to TiO₂ nanoparticles (Herath, Perera and Hettiarachchi, 2020). This composite of TiO₂/N719 demonstrated an outstanding rapid photocatalytic activity on removal of methylene blue (MB) under visible light which was stable and reusable. However, N719 dye is very expensive and it desorbed from TiO₂ under strongly basic conditions. Therefore, much cheaper and stable dye based composite was investigated to develop a new visible light photocatalyst.

Herein we report the synthesis of a new TiO₂ composite with brilliant yellow dye (C₂₆H₁₈N₄Na₂O₈S₂) following the same solvothermal one-pot synthesis technique. The uniqueness of this composite (Ti-BY) is that it exhibits not only the photocatalytic activity but also it acts as an adsorbent in dye removal process.

MB was used to demonstrate the dual functionality of the Ti-BY composite. MB is a highly neurotoxic commonly used synthetic cationic dye in various industries (Oz *et al.*, 2011).

MATERIALS AND METHODS

Chemicals

All chemicals and reagents were purchased from Sigma Aldrich except brilliant yellow dye (C₂₆H₁₈N₄Na₂O₈S₂) (HOPKIN & WILLIAMS Ltd) and were used as received without further purification.

Synthesis of Ti-BY composite

Brilliant yellow (1.00 mmol) dissolved in 5.00 mL of DMF was added drop-wise to 2.00 mL of acetic acid while stirring. Then, 0.30 mL (1.00 mmol) of titaniumisopropoxide was added to this solution. The solution was transformed into a 23 mL Teflon lined autoclave reactor and heated in an oven at 145 °C for 84 h. The brown product was filtered under

*Corresponding Author's Email: ishanieperera@sci.pdn.ac.lk, ishanie.arachchige@gmail.com



<https://orcid.org/0000-0003-4297-5028>

vacuum and soaked in ethanol for three days by replacing the solvent each day with fresh solvent. Finally, the product was air dried.

Characterization

SHIMADZU IR Prestige 21 spectrometer with a KBr Beam splitter and a DLaPGS detector was used to record the FT-IR absorbance spectra using KBr pellets with 1wt% sample.

UV-1800 SHIMADZU spectrophotometer was used to record UV-visible spectra at slow scan rate in auto scan mode. Compound was characterized qualitatively using SIEMENS D5000 diffractometer equipped with a Cu target metal and a Ni K_β filter in the scan range of (2θ) 5°- 40° with the step size of 0.02° operated at 25 kV and 40 mA.

For Ion Chromatography Metrosep A Supp 5 - 250/4.0 column that composed of Anion Eluent - 3.2 mM Na₂CO₃ + 1.0 mM NaHCO₃ (678 mg Na₂CO₃ + 168 mg NaHCO₃ into 2 L UPW) was used with a flow rate of 0.700 mL/min at 11.42 MPa pressure and at 30 °C temperature.

Adsorption and photocatalytic experiments

Aliquots of 10.00 mL MB solution (0.025 mmol dm⁻³) were taken into 20 mL beakers and 0.020 g of finely powdered Ti-BY was added to each MB solution. Solutions were then kept in the dark for 1 h to achieve the equilibrium. The adsorption experiments were conducted under dark, sunlight (0.7321 W m⁻²), white LED light (power-12 W, Luminous Flux- 1000 lm, colour- 6500 K ± 450K) and ambient conditions. Absorbance measurements were recorded after 2 h at λ_{max} = 664 nm (Completion of the adsorption/photocatalysis at 2 h was determined by checking the absorbance of the test solution in every 20 min for 3 h). All experiments were carried out in triplicates. One beaker containing only TiO₂ (0.020 g) with MB was kept under the dark condition and another beaker with TiO₂ (0.020 g) and MB was irradiated with sunlight as controls.

The percentage removal of dye was calculated using equation (1).

$$\% \text{ removal} = \frac{A_i - A_t}{A_i} \times 100 \quad (1)$$

where, A_i is the initial absorption of the dye and A_t is the absorption of the dye at time "t".

Optimization of pH

Aliquots of 10.00 mL MB solution (0.025 mmol dm⁻³) were taken into 20 mL beakers and 0.020 g of finely powdered Ti-BY was added to each MB solution. The pH (2 to 12) of the solutions was adjusted using HNO₃ and NaOH. Solutions were then kept in the dark for 1 h to achieve the equilibrium. The absorbance of each solution was recorded at λ_{max} = 664 nm after 2 h irradiation with sunlight.

Desorption experiments

Dye adsorbed Ti-BY composite (0.020 g) was taken into 20 mL beaker and 10.00 mL of 5.00 mol dm⁻³ HCl was added. The solution was kept for three days while stirring. The UV-Vis absorption data of the desorbed solution

was measured on each day. Then, on the third day, the compound was washed with a mixture of water and 1.00 mol dm⁻³ NaOH solution. Concentrations of desorbed MB dye in HCl washings were determined using UV Visible spectroscopy at the λ_{max} value of 664 nm.

RESULTS AND DISCUSSION

Characterization

Using the solvothermal one-pot synthesis technique, a brown thermally stable TiO₂/brilliant yellow composite (Ti-BY) having a melting point above 350 °C was obtained. Figure 1 depicts the PXRD patterns of Ti-BY and brilliant yellow dye (BY). The formation of Anatase phase TiO₂ was confirmed by the peaks appearing at 2θ values of 24.8°, 37.3°, 47.6°, 53.5°, 55.1° and 62.2° (JCPDS Card no. 21-1272) in the PXRD pattern of Ti-BY [Figure 1(b)] (Anandhi *et al.*, 2016). Further, the additional peak at 2θ value of 32.1° in the PXRD pattern of Ti-BY corresponds to the major peak in BY dye which confirmed the presence of BY dye as well, and thereby the formation of a composite. However, broader PXRD peaks with some noises indicate the presence of TiO₂ and dye with poor crystallinity.

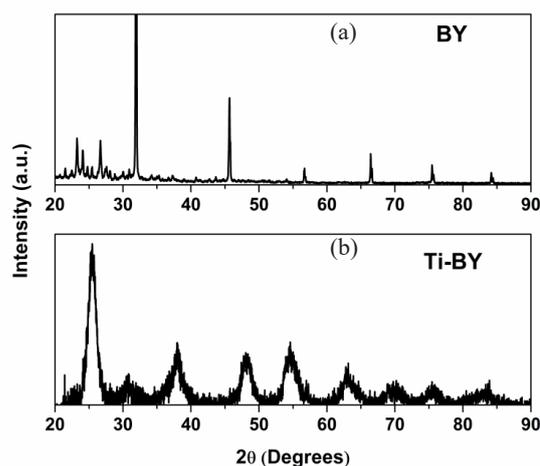


Figure 1: PXRD patterns of (a) brilliant yellow dye and (b) Ti-BY composite.

FT-IR spectra of Ti-BY and BY dye and the chemical structure of BY are shown in Figure 2 (a) and (b) respectively. In both spectra, the broad band maximising at 3471 cm⁻¹ corresponds to the vibration frequency of O-H bonds providing a direct evidence of unaffected O-H groups of BY remaining in the composite. Bands appearing at 1508 cm⁻¹ in both spectra can be assigned to the vibrations of the C=C bonds in benzene rings (Abedi *et al.*, 2015). ZnO/GAC, and TiO₂-ZnO/GAC combined with non-thermal plasma (NTP). Moreover, the asymmetric stretching vibration of S=O bond is responsible for the prominent absorption band appearing at 1477 cm⁻¹ in BY, while less noticeable in Ti-BY. Further, the peak at 1080 cm⁻¹ in the BY corresponds to the symmetric stretching vibration of S-O bond which disappeared in the spectrum of Ti-BY. These evidences clearly imply the formation of a metal-ligand bond between group in BY and Ti(IV) in TiO₂ particles. The broad band appearing at 667 cm⁻¹ in

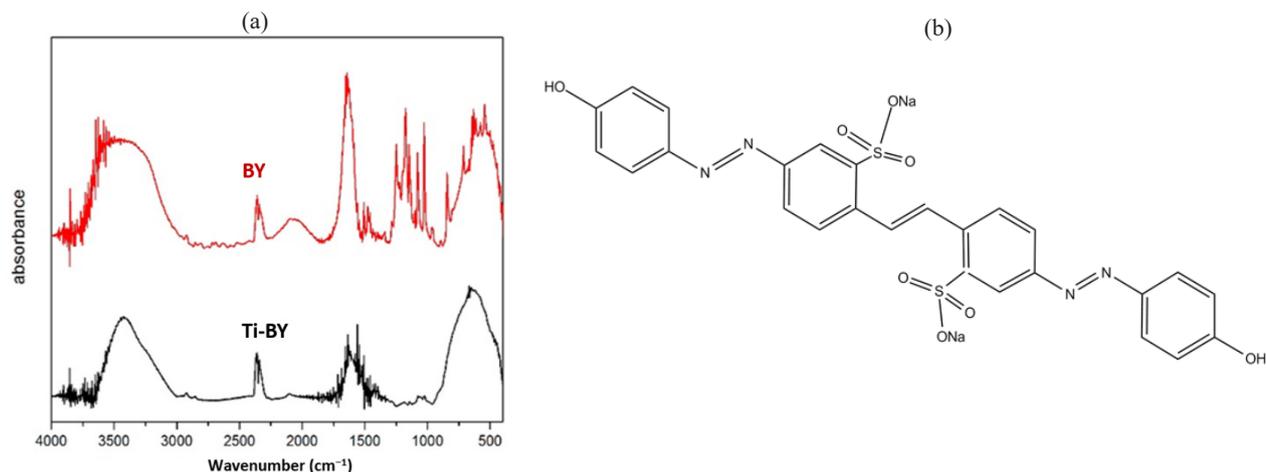


Figure 2: (a) FT-IR spectra of BY and Ti-BY and (b) chemical structure of BY.

Ti-BY spectrum may prove the formation of S-O-Ti bonds. Also the strong peak appearing around 1643 cm^{-1} in BY spectrum has shifted to the 1635 cm^{-1} in Ti-BY as a weak peak indicating the presence of N=N bond, but, shifted to a lower value due to the formation of S-O-Ti bond (Moussa, 2000).

Photocatalytic and adsorption activity

Initially, to optimize the mass of the Ti-BY needs to be used in photocatalytic and adsorption activity efficiently, the amount of composite was changed from 5.0 mg to 25.0 mg upon sunlight irradiation. Accordingly, dye removal efficiency increased from 74% to 86% in 5.0 mg to 20.0 mg respectively, whereas after 20.0 mg, the efficiency was not changed significantly. Thus, 20.0 mg of Ti-BY was used as the optimum mass for further dye removal experiments.

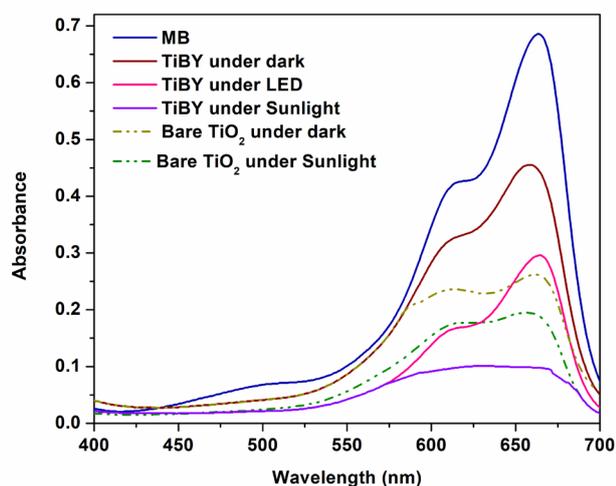


Figure 3: UV-visible absorption spectra of $0.025\text{ mmol dm}^{-3}$ methylene blue aqueous solutions without Ti-BY, after 2 h in contact with TiO_2 under dark and sunlight, after 2 h in contact with Ti-BY under dark, sunlight and an artificial light.

Figure 3 depicts the UV-visible absorption spectra of $0.025\text{ mmol dm}^{-3}$ MB solution in contact with Ti-BY under dark, sunlight and an artificial white light irradiation after 2 h showing 45%, 86% and 79% removal efficiencies respectively. Thus, the removal efficiency observed under dark conditions (45%) must be due to only the adsorptive

removal of MB. Irradiation with LED white light has increased the efficiency from 45% to 79% which must be due to the photocatalytic removal by Ti-BY along with the adsorption. The photocatalytic activity of Ti-BY was further confirmed by ion chromatography data recorded for the dye solution after 2 h. Appearance of peaks corresponding to nitrate and sulfate confirmed clearly the degradation of some amount of MB photocatalytically as well (Herath, Perera and Hettiarachchi, 2020).

The presence of brilliant yellow dye in the composite allows TiO_2 particles to absorb visible light and the mechanism is as indicated in the Figure 4. In the composite, dye and the semiconductor work together but as two units. Dye molecules absorb visible light and due to photoexcitation, they inject electrons to the CB of the semiconductor. These photogenerated species will initiate the photo degradation of the pollutant.

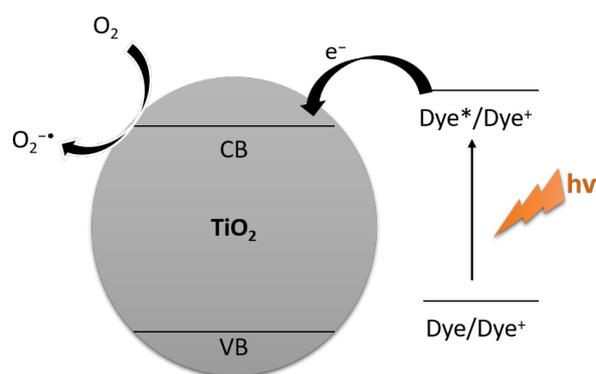


Figure 4: Schematic diagram of the mechanism of photocatalysis by Ti-BY composite.

Conversely, when the reaction mixture was exposed to sunlight, the dye removal efficiency further increased to 86% (Figure 3) due to the presence of UV component in the sunlight. Thus, other than the adsorptive removal and photocatalysis initiated by the visible radiation, TiO_2 nanoparticles themselves have undergone the photocatalysis upon UV irradiation. The spectrum in the LED bulb covers only the visible region without UV component. Thus, the efficiency under LED light is lower than that of under sunlight. Hence, all three phenomena;

adsorption, photocatalysis by both visible and UV energies were observed under sunlight demonstrating the highest dye removal efficiency.

The dye removal efficiency was further optimized by conducting the experiments from pH 2-12 upon sunlight irradiation (Figure 5). Accordingly, high efficiencies were observed in basic pHs and the maximum performance of 97% removal was observed at pH 11. In basic pHs, the deprotonation of terminal OH groups of BY which were unaffected by the composite formation and surface OH groups of TiO₂ could be enhanced. This facilitated a better adsorption of cationic MB molecules to the composite leading to higher dye removal efficiency in the basic medium. When the bare TiO₂ was used, only 82% of the MB dye was removed at pH 11 upon sunlight irradiation. This clearly indicates the improvement gained by utilizing the Ti-BY composite for MB removal.

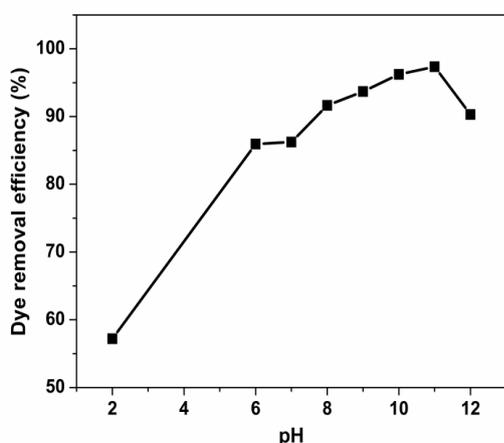


Figure 5: Effect of pH on the adsorption of MB dye at pH range from 2-12.

In the adsorption studies, the colour of the Ti-BY composite changed from brown to green and the original brown colour was regenerated by desorbing the MB from the composite using a 5.00 mol dm⁻³ HCl solution. This allowed the Ti-BY composite to be reused in dye removal process. The efficacies in reusability of the composite tested for three dye removal cycles were found as 97%, 94% and 91% for cycle 1, 2 and 3 respectively. Even in the third cycle, the dye removal percentage by Ti-BY remained above 90% implying the excellent reusability. Further, the total average desorbed amounts of MB were calculated based on UV-Visible spectroscopic data as 0.014 ± 0.004 mmol dm⁻³ for three trials. This further proved thoroughly that ~56% of the MB has been adsorbed to the composite at pH 11 and the remaining dye amount must have been photocatalytically degraded. This was further confirmed with the support of IC data collected for the reaction mixture after 2 h on white light irradiation. Accordingly, MB molecules have also photocatalytically been degraded to sulfates and nitrates by the composite.

According to the literature, only a limited number of reports have been published on dye-sensitized TiO₂ as a photocatalyst for the synthetic dye degradation process. On the other hand, the degradation of sensitizing dye gradually

via a self-sensitized photocatalytic process, the desorption of the sensitized dye at high pHs and a slow photocatalytic degradation process were the main drawbacks reported in those systems (Chatterjee *et al.*, 2006; Jiang *et al.*, 2008). Comparingly, Ti-BY composite is stable even at high pH values and free from self-degradation. Most importantly, these efficiencies were obtained in the absence of H₂O₂ which indicates that when H₂O₂ is used, 100% removal of MB can be achieved within less than 2 h.

CONCLUSIONS

In conclusion, Ti-BY composite was successfully synthesized under solvothermal conditions using one-pot synthesis method. This composite was found to be active under dark conditions as well as under irradiation with sunlight owing to the excellent dual functionality. Two dye removal processes, adsorptive removal and photocatalytic dye degradation were observed using the Ti-BY composite on methylene blue. Optimized system of Ti-BY demonstrated a dye removal percentage of 97% at pH 11 after 2 h of irradiation with sunlight without H₂O₂. Further, the Ti-BY composite exhibited more than 90% dye removal capability even in the third dye removal cycle. Thus, Ti-BY may be an outstanding composite suitable to be utilized in removal of methylene blue from industrial effluents with an excellent reusability.

ACKNOWLEDGEMENT

Authors would like to thank the University of Peradeniya Grant, URG/2017/46/S, for the financial assistance.

DECLARATION OF CONFLICT OF INTEREST

The authors declare no competing interests.

REFERENCES

- Abedi, K., Ghorbani-Shahna, F., Jaleh, B., Bahrami, A., Yarahmadi, R., Haddadi, R. and Gandomi, M. (2015). Decomposition of chlorinated volatile organic compounds (CVOCs) using NTP coupled with TiO₂/GAC, ZnO/GAC, and TiO₂-ZnO/GAC in a plasma-assisted catalysis system. *Journal of Electrostatics* **73**: 80-88. DOI: <https://doi.org/10.1016/j.elstat.2014.10.008>.
- Anandhi, A., Palraj, S., Subramanian, G. and Selvaraj, M. (2016). Corrosion resistance and improved adhesion properties of propargyl alcohol impregnated mesoporous titanium dioxide built-in epoxy zinc rich primer. *Progress in Organic Coatings* **97**: 10-18.
- Babuponnusami, A. and Muthukumar, K. (2014). A review on Fenton and improvements to the Fenton process for wastewater treatment. *Journal of Environmental Chemical Engineering* **2**(1): 557-572. DOI: 10.1016/j.jece.2013.10.011.
- Chatterjee, D., Dasgupta, S., Dhodapkar, R.S. and Rao, N.N. (2006). Simultaneous degradation of non-emissive and emissive dyes on visible light illuminated TiO₂ surface. *Journal of Molecular Catalysis A: Chemical* **260**(1): 264-268. <http://neeri.csircentral.net/id/eprint/50>.
- Crini, G. (2006). Non-conventional low-cost adsorbents for dye removal: A review. *Bioresource Technology*

- 97(9): 1061-1085. DOI : <https://doi.org/10.1016/j.biortech.2005.05.001>.
- Forgacs, E., Cserhati, T. and Oros, G. (2004). Removal of synthetic dyes from wastewaters: a review. *Environment International* **30**(7): 953-971.
- Haque, E., Jun, J.W. and Jhung, S.H. (2011). Adsorptive removal of methyl orange and methylene blue from aqueous solution with a metal-organic framework material, iron terephthalate (MOF-235). *Journal of Hazardous Materials* **185**(1):507-511.DOI: 10.1016/j.jhazmat.2010.09.035.
- Hussain, S.M., Hussain, T., Faryad, M., Ali, Q., Ali, S., Rizwan, M., Hussain, A.I., Ray, M. B. and Chatha, S.A.S. (2021).Emerging Aspects of Photo-catalysts (TiO₂& ZnO) Doped Zeolites and Advanced Oxidation Processes for Degradation of Azo Dyes: A Review *Current Analytical Chemistry* **17**(1): 82-97. DOI:10.2174/1573411016999200711143225.
- Herath, I., Perera, I. and Hettiarachchi, H (2020). One-pot synthesis of highly dye impregnated TiO₂ nanoparticles for improved white light photo-degradation. *Pigment and Resin Technology* **49**(1): 1-10. DOI:<https://doi.org/10.1108/PRT-03-2019-0031>.
- Jamee, R. and Siddique, R. (2019). Biodegradation of Synthetic Dyes of Textile Effluent by Microorganisms: An Environmentally and Economically Sustainable Approach. *European Journal of Microbiology and Immunology* **9**(4): 114-118. DOI: 10.1556/1886.2019.00018.
- Jiang, C. and Zhang, J. (2007). Progress and prospect in electro-Fenton process for wastewater treatment. *Journal of Zhejiang University-SCIENCE A* **8**(7): 1118-1125. DOI: <https://doi.org/10.1631/jzus.2007.A1118>.
- Jiang, D., Xu, Y., Wu, D. and Sun, Y. (2008). Visible-light responsive dye-modified TiO₂ photocatalyst. *Journal of Solid State Chemistry* **181**(3): 593-602. DOI: 10.1016/j.jssc.2008.01.004.
- Ramakrishnan, K., Padil, R., Waclawek, V.V.T., S., ˇCernık, M. and Varma R.S. (2021). Eco-Friendly and Economic, Adsorptive Removal of Cationic and Anionic Dyes by Bio-Based Karaya Gum-Chitosan Sponge. *Polymers* DOI : <https://doi.org/10.3390/polym13020251>.
- Lellis, B., Favaro-Polonio, C.Z., Pamphile, J.A. and Polonio, J.C. (2019). Effects of textile dyes on health and the environment and bioremediation potential of living organisms. *Biotechnology Research and Innovation* **3**(2): 275-290. DOI: <https://doi.org/10.1016/j.biori.2019.09.001>.
- Miranda-Garcıa, N., Suarez, S., Sanchez, B., Coronado, J.M., Malato, S. and Maldonado, M.I. (2011). Photocatalytic degradation of emerging contaminants in municipal wastewater treatment plant effluents using immobilized TiO₂ in a solar pilot plant. *Applied Catalysis B: Environmental* **103**(3): 294-301. DOI: 10.1016/j.apcatb.2011.01.030.
- Moussa, N.A. (2000). Physicochemical and Textural Characterization of Perchlorated and Persulphated Titania. *Adsorption Science and Technology* **18**(9): 839-850. DOI:<https://doi.org/10.1260/0263617001493855>.
- Oz, M., Lorke, D.E., Hasan, M. and Petroianu, G.A. (2011). Cellular and molecular actions of methylene blue in the nervous system. *Medicinal Research Reviews* **31**(1): 93-117. DOI: 10.1002/med.20177.
- Sharma, K., Dalai, A.K. and Vyas, R.K. (2018). Removal of synthetic dyes from multicomponent industrial wastewaters. *Reviews in Chemical Engineering* **34**(1): 107-134. DOI: <https://doi.org/10.1515/revce-2016-0042>.
- Shindhal, T., Rakholiya, P., Varjani, S., Pandey, A., Ngo, H.H., Guo, W., Ng, H.Y. and Taherzadeh, M. J. (2021). A critical review on advances in the practices and perspectives for the treatment of dye industry wastewater. *Bioengineered* **12**(1): 70-87. DOI:<https://doi.org/10.1080/21655979.2020.1863034>.
- Sing, K.S.W. (1998). Adsorption methods for the characterization of porous materials. *Advances in Colloid and Interface Science* **76-77**: 3-11.
- Sriramoju, J.B., Muniyappa, M., Marilingaiah, N.R., Sabbanahalli, C., Shetty, M., Mudike, R., Chitrananu, C.P., Prasanna, D. S., Nagaraju, G, Kanchugarakoppal, S. R., Ananda, K.C.S., Dinesh, R. (2021). Carbon-based TiO₂-x heterostructure nanocomposites for enhanced photocatalytic degradation of dye molecules. *Ceramics International* **47**(7) Part B: 10314-10321. DOI: 10.1016/j.ceramint.2020.12.014.
- Yaseen, D.A. and Scholz, M. (2019). Textile dye wastewater characteristics and constituents of synthetic effluents: a critical review. *International Journal of Environmental Science and Technology* **16**: 1193-1226. DOI:<https://doi.org/10.1007/s13762-018-2130-z>.
- Yu, K.L., Lee, X.J., Ong, H.C., Chen, W.H., Chang, J.-S., Lin, C.-S., Show, P.L. and Ling T.C. (2021). Adsorptive removal of cationic methylene blue and anionic Congo red dyes using wet-torrefied microalgal biochar: Equilibrium, kinetic and mechanism modeling. *Environmental Pollution* **272**: 115986. DOI: <https://doi.org/10.1016/j.envpol.2020.115986>.
- Al Zoubi, W., Salih Al-Hamdani, A.A., Sunghun, B. and Ko, Y.G. (2021). A review on TiO₂-based composites for superior photocatalytic activity. *Reviews in Inorganic Chemistry*, DOI : <https://doi.org/doi:10.1515/revic-2020-0025>.