PHOTOCATALYTIC DEGRADATION OF DYES USING SURFACE MODIFIED SEMICONDUCTORS

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SYNOPSIS

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General Introduction

Organic dyes that are emitted from various sources pose severe ecological problem, as the bio-degradation of these pollutants is often very slow and the conventional treatment is mostly ineffective and not environmentally compatible. In this regard, the application of photocatalysis, especially photocatalysis using semiconductor system, appears to be the most appealing mean than the more conventional chemical oxidation methods for decomposition of toxic compounds to non-hazardous products. This is because of the fact that semiconductors are inexpensive, non-toxic, possessing a high surface area, having broad absorption spectra with high absorption coefficients, exhibiting tunable properties which can be modified by size reduction, doping, sensitizers, *etc.,* affording facility for multi electron transfer process and capable of extended use without substantial loss of photocatalytic activity. However, the photocatalytic efficiency of semiconductors (TiO_2 and ZnO) to degrade dyes decreases substantially due to the high recombination ratio of photo-induced electrons (e^-) and holes (h^+) produced when irradiated under ultraviolet light.. In addition, for TiO_2 and ZnO the threshold or ideal wavelength corresponding to the band-gap energy of 3.02 eV is at near ultraviolet radiation. Thus the technological utility of this process is restricted to limited applications due to the need of an UV excitation source. This fact has profoundly influenced research in photocatalysis, so that modification of TiO_2 and ZnO materials to achieve efficient photoactivation in the visible spectrum is an active field of research.

Scope of the present Investigation

In the perspective, even though there are already a number of reports on photocatalysts of TiO_2 based nanocomposites, but it is still a challenge for further enhancing their photoactivity under UV/solar light irradiation. Therefore, novel and environmental-friendly approaches for the fabrication of surface modified TiO_2 based hybrid nanocomposite photocatalyst remain a great challenge. ***Thus, the scope of the present investigation is to develop effective photocatalysts with high catalytic efficiency for the degradation of dyes under UV and solar irradiations.***

Aims and Objectives of the present study

The aim and objectives of the present investigations are as follows:

- *To synthesis/fabricate TiO_2 based nanocomposites viz., TiO_2-Graphene (TiO_2-GR), TiO_2-Poly o-phenylenediamine (TiO_2-PoPD) and TiO_2-Commercial activated carbon (TiO_2-CAC) by simple chemical method.*
- *To study the structure of TiO_2-GR, TiO_2-PoPD and TiO_2-CAC nanocomposites using Ultra Violet visible spectroscopy (UV-Vis), Fourier Transform Infra Red (FT-IR), Raman spectroscopy and X-Ray Diffraction (XRD) studies.*
- *To characterize the morphology of TiO_2-GR, TiO_2-PoPD and TiO_2-CAC nanocomposites by Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) measurements*
- *To investigate the thermal stability of the as prepared nanocomposites using Thermogravimetric Analysis (TGA)*
- *To examine the photo catalytic degradation of two different commercial organic dyes [Acid Orange 7 (AO7) and Rhodamine B (RhB)] using TiO_2-GR, TiO_2-PoPD and TiO_2-CAC nanocomposites catalyst under UV and Solar irradiations*

- *To study the different process parameters like Effect of Initial Concentration, Contact time, Dose of the Catalyst and pH of dyes solution under UV and Solar irradiations using TiO_2-GR, TiO_2-PoPD and TiO_2-CAC nanocomposites*
- *To determine the rate of reaction for the removal of substrates by photocatalysis*
- *To analyze the degradation products by Mass Spectral studies and predict the mechanism as well as degradation pathway of dyes.*

Chapter 1: Introduction

This chapter deals with general introduction to water pollution, various root causes of water pollution especially from industries such as dye, heavy metals and toxic/hazardous chemicals. Various methods of wastewater treatment in general and for removal of dyes, in particular by photocatalysis also presented. The salient features involved in the disciplines of photocatalysis are presented in this chapter. In addition to these, introduction about semiconductors, dyes and surface modified titanium dioxide nanocomposites have also been given in detail.

Chapter 2: Review of Literature

This chapter contains detailed review of literature on the studies of fabrication methods and characterization techniques used for surface modified photocatalysts. Moreover, detailed investigation on the photocatalytic degradation of various dyes under UV and solar irradiations also given in detail. In addition, a short summation of the current literature on the topic has been presented as well. At the end, need and scope followed by aims and objectives of the present investigation are discussed.

Chapter 3: Experimental Methodology

Experimental methods comprise the description of all chemicals and reagents used for the experimental work. Optical studies have been carried out by UV-vis spectroscopic technique, whereas the structural studies have been recorded using Fourier Transform Infrared (FTIR) and X-ray Diffraction (XRD), Raman, BET measurements. The surface morphology of the surface modified semiconductor nanocomposite photocatalyst was examined by electron microscopic techniques like FESEM, HRTEM and AFM. The electrochemical performances were successfully studied by CV and EIS studies. The photodegradation experiments were carried out in a 150 ml cylindrical glass reactor (HEBER Multilamp Type Photoreactor) equipped with an UV lamp (365 nm). The concentration of residual AO7 and RhB dyes were determined by visible spectrophotometer (ELICO SL 207 MINI SPEC) based on the absorbance at the wavelength of 483 nm. The pH of the dye solution was measured by using digital pen pH meter (Hanna instrument, Portugal). The technical details for all the instrumental measurements carried out for the investigations are presented in this chapter.

Results and Discussion

This chapter discussed the synthesis, fabrication, characterization and photocatalytic degradation of two different dyes under UV and solar irradiations.

Chapter 4: ***Fabrication and characterization of TiO_2-graphene nanocomposites for Acid Orange 7 and Rhodamine B dyes degradation under solar/UV light irradiations***

Environmental friendly, effective route for easy and cost-effective strategy was adopted for the fabrication of TiO_2-GR nanocomposite based hybrid nanocomposite by simple one step chemical process. HRTEM and FESEM analysis revealed that the TiO_2 nanoparticles are uniformly decorated on the GR surface. Microscopy studies also confirmed that the incorporation of TiO_2 nanoparticles on the GR surface. Spectroscopic studies (FTIR, Raman, XRD, BET and UV-DRS) evinced that the optimal assembly and interfacial coupling between the GR sheets and TiO_2 in TiO_2-GR nanocomposite. Electrochemical studies showed that the TiO_2-GR nanocomposite possess greater red-ox activity and electrical conductivity than the TiO_2 alone. TGA studies showed that the TiO_2-GR nanocomposite possesses more thermal stability when compared to TiO_2. Photodegradation studies showed that, the percentage removal of dyes (AO7 and RhB) on TiO_2-GR nanocomposite catalyst under the UV/solar irradiation was found to decrease with the increase in initial concentration of dye, which is due to the lake of available active sites. Moreover, the extent of removal of dyes was found to increase with increase in contact time and dose of the catalysts. The photocatalytic degradation of dyes (AO7 and RhB) under the UV/solar irradiation followed pseudo-first-order kinetics according to the Langmuir–Hinshelwood model. The percentage removal of dye (AO7) decreased with increase in the initial pH of the dye solution but the percentage removal increased with increase in the initial pH of the RhB dye solution.

Though the UV irradiation can bring better efficiency in the degradation of AO7, solar energy will emerge as an alternative cost effective light source because of its abundance and non-hazardous nature.

Chapter 6: ***Facile Synthesis, Characterization and photocatalytic degradation studies of TiO_2@Poly(o-phenylenediamine) Nanocomposites for Acid Orange 7 and Rhodamine B dyes under UV irradiation***

In-situ chemical oxidative polymerization method was adopted first time for the preparation of TiO_2@PoPD core-shell nanocomposites. The TEM and AFM analysis confirms the core-shell features of TiO_2@PoPD nanocomposites. UV–*vis* DRS spectra showed that TiO_2-PoPD core-shell nanocomposites have a broad and strong absorption in visible range, indicating that the incorporation of PoPD onto the surface of TiO_2 can extend the photo response range of TiO_2. TGA studies showed that the TiO_2-PoPD nanocomposite possesses more thermal stability when compared to PoPD. Photocatalytic activities of PoPD@TiO_2 nanocomposites on AO7 and RhB dyes were remarkably improved than TiO_2 in UV light. Photodegradation studies revealed that, the percentage removal of dyes dyes on TiO_2-CAC nanocomposite under the UV irradiation was found to decrease with the increase in initial concentration of dye and increase with increase in contact time and dose of the catalysts. The photocatalytic degradation of dyes (AO7 and RhB) was followed pseudo-first-order kinetics according to the Langmuir–Hinshelwood model. The percentage removal of dye (AO7) decreased with increase in the initial pH of the dye solution but the percentage removal increased with increase in the initial pH of the RhB dye solution. Based upon the synergetic effect between PoPD and TiO_2, a rapid charge separation and slow charge recombination came true in both the visible and ultraviolet radiations.

It is hoped that our work could provide valuable information on the design of polymer modified semiconductor with more excellent properties and set the foundation for the further industrial application.

Chapter 7: ***Preparation, Characterization and Photocatalytic degradation studies of CAC-TiO_2 nanocomposites for mineralization of acid orange 7 and Rhodamine B dyes under UV irradiation***

The CAC-TiO_2 composite was prepared by simple chemical route and the as prepared composite was characterized using Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD) and Thermo gravimetric analysis. The photodegradation efficiency of the CAC-TiO_2 composite was eighteen order magnitudes higher than that of pure TiO_2 for AO7 and RhB dyes degradation. Photodegradation studies revealed that, the percentage removal of dyes dyes on TiO_2-CAC nanocomposite under the UV irradiation was found to decrease with the increase in initial concentration of dye and increase with increase in contact time and dose of the catalysts. The photocatalytic degradation of dyes (AO7 and RhB) was followed pseudo-first-order kinetics according to the Langmuir–Hinshelwood model. The percentage removal of dye (AO7) decreased with increase in the initial pH of the dye solution but the percentage removal increased with increase in the initial pH of the RhB dye solution.

The total mineralization of dyes, through the combination of adsorption and degradation was achieved in a reasonable time, and can therefore be suggested as an efficient, cost-effective and environment friendly water treatment methodology.

Chapter 8: ***Photodegradation Pathway, Mechanism, Efficiency Comparison and Reusability studies***

In this chapter, identification of the mineralization (intermediate) products by GC–MS analysis was employed and the intermediate products identified for AO7 and RhB dyes under UV irradiations. Overall, results of the present study show that photocatalytic treatment of the dyes-catalyst system with UV irradiation may lead to

oxidative fragmentation of the dye molecule toward colourless compounds of progressively lower molecular weight and, eventually, to CO_2 and inorganic ions. Based on the results and previous studies, a plausible degradation mechanism was also proposed.

Comparison on the photo catalytic degradation ability of as prepared surface modified TiO_2 photocatalyst *viz.,* TiO_2–GR, TiO_2–PoPD and TiO_2–CAC nanocomposites on AO7 and RhB dyes were investigated under UV irradiation in optimum condition. Based on the first order rate constant (k/min.) values the degradation efficiency is as follows: ***TiO_2–GR ≥ TiO_2–PoPD >> TiO_2–CAC nanocomposites.***

Reusability/photostability studies proved that, TiO_2-GR nanocomposite is reusable photocatalyst for the degradation of dyes. The reused catalyst does not show any noticeable change in the degradation efficiency which emphasizes the excellent photochemical stability and reusability of the catalysts that is beneficial for practical application.

CONCLUSIONS

The present study deals with the decolorisation dyes (AO7 and RhB) on surface modified semiconductors (TiO_2–GR, TiO_2–PoPD and TiO_2–CAC nanocomposites) by photo catalytic degradation technique. Surface morphology and structural features of the nanocomposites were characterized by various methods. The effect of initial concentration (C_i), contact time, dose of the catalyst and initial pH of the dye solution on the extent of removal (%R) of dyes were studied by photo catalytic degradation technique and the following conclusions which were arrived at from the results :

- ☞ Environmental friendly, effective route for easy and cost-effective strategy was adopted for the fabrication of TiO_2–GR, TiO_2–PoPD and TiO_2–CAC nanocomposites by simple one step chemical process.
- ☞ Microscopy studies (HRTEM, FESEM and AFM) confirmed the formation of above said TiO_2 based hybrid nanocomposites.
- ☞ Spectroscopic studies (UV-DRS, FTIR, Raman, XRD evinced that the optimal assembly and interfacial coupling between the GR, PoPD and CAC with TiO_2 nanoparticles.
- ☞ Electrochemical studies showed that the TiO_2–GR nanocomposites possess enhanced redox activity and electrical conductivity.
- ☞ Thermal studies (TGA) proved that the as prepared nanocomposites possess greater thermal stability than the pure materials *viz.,* GR, PoPD and CAC.
- ☞ Photodegradation studies showed that, the percentage removal of dyes (AO7 and RhB) on these nanocomposite catalysts under UV/solar irradiations were found to decrease with the increase in initial concentration of dye, which is due to the lake of available active sites.

    1. The extent of color removal of dyes by photo degradation on nanocomposite catalysts was found to increase with increase in contact time for both the dyes. The first order kinetic equation (Langmuir–Hinshelwood) was found to be applicable in the present dye–catalyst systems.
    2. The percentage removal of dyes was increased exponentially with the increase in dose of catalysts.
    3. The percentage color removal of AO7 dye increased with decrease in the initial pH of the solution for all three nanocomposite catalysts. In contrast, the percentage removal of RhB dye increased with increase in the initial pH of the

solution for all three nanocomposite catalysts. This may be due to the acidic and basic nature of dyes.

- Photodegradation studies proved that TiO_2–GR, TiO_2–PoPD and TiO_2–CAC nanocomposites possessed greater efficiency for both dyes *viz.,* AO7 and RhB compared to TiO_2 alone due to the electron transfer between TiO_2 and GR will greatly retard the recombination of photoinduced charge carriers and prolong electron lifetime, which contribute to the enhancement of photocatalytic performance.
- Though the UV irradiation can bring better efficiency in the degradation of dyes (AO7 and RhB), solar energy will emerge as an alternative cost effective light source because of its abundance and non-hazardous nature.

The results of this research highlighted new insight into the fabrication of the nanocomposites (TiO_2–GR, TiO_2–PoPD and TiO_2–CAC) as a high performance UV-light responsive catalyst and facilitates its application in environmental protection issues.

REFERENCES

1. H. Park, Y. Park, W. Kim, W. Choi, Surface modification of TiO_2 photocatalyst for environmental applications-Invited review, Journal of Photochemistry Photobiology C: Photochemistry Review 15 (2013) 1– 20.
2. B.T. Zhang, X. Zheng, H.F. Li, J.M. Lin, Application of carbon-based nanomaterials in sample preparation: A review, Analytica Chimica Acta 784 (2013) 1–17.
3. R. Leary, A. Westwood, Carbonaceous nanomaterials for the enhancement of TiO_2 photocatalysis, Carbon 49 (2011) 741–72.
4. X. An, J.C. Yu, Graphene-based photocatalytic composites, RSC Advances 1 (2011) 1426–1434.
5. S. Kaveri, L. Thirugnanam, M. Dutta, J. Ramasamy, N. Fukata, Thiourea assisted one-pot easy synthesis of CdS/rGO composite by the wet chemical method: Structural, optical, and photocatalytic properties, Ceramics International 39 (2013) 9207-9214.
6. Q. Xiang, J. Yu, M. Jaroniec, Graphene-based semiconductor photocatalysts, Chemical Society Reviews 41 (2012) 782–796.
7. H. Raj Pant, B. Pant, H. Joo Kim, A. Amarjargal, C. Hee Park, L. D. Tijing, E. Kyo Kim, C. Sang Kim, A green and facile one-pot synthesis of Ag–ZnO/RGO nanocomposite with effective photocatalytic activity for removal of organic pollutants, Ceramics International 39 (2013) 5083-5091.
8. X.S. Zhou, F. Peng, H.J. Wang, H. Yu, Y.P. Fang, A simple preparation of nitrogen doped titanium dioxide nanocrystals with exposed (001) facets with high visible light activity, Chemical Communications 48 (2012) 600–602.

9. G.D. Jiang, Z.F. Lin, C. Chen, L.H. Zhu, Q. Chang, N. Wang, TiO_2 nanoparticles assembled on graphene oxide nanosheets with high photocatalytic activity for removal of pollutants, Carbon 49 (2011) 2693–2701.

10. X.Y. Zhang, H.P. Li, X.L. Cui, Y.H. Lin, Graphene/TiO_2 nanocomposites: synthesis, characterization and application in hydrogen evolution from water photocatalytic splitting, Journal of Materials Chemistry 20 (2010) 2801–2806.

11. J.F. Shen, B. Yan, M. Shi, H.W. Ma, N. Li, M.X. Ye, One step hydrothermal synthesis of TiO_2-reduced graphene oxide sheets, Journal of Materials Chemistry 21 (2011) 3415–3421.

12. J.F. Shen, M. Shi, B. Yan, H.W. Ma, N. Li, M.X. Ye, Ionic liquid assisted one-step hydrothermal synthesis of TiO_2-reduced graphene oxide composites, Nano Research 4 (2011) 795–806.

13. X.Y. Zhang, Y.J. Sun, X.L. Cui, Z.Y. Jiang, A green and facile synthesis of TiO_2/graphene nanocomposites and their photocatalytic activity for hydrogen evolution. International Journal of Hydrogen Energy 37 (2012) 811–815.

14. H.J. Zhang, P.P. Xu, G.D. Du, Z.W. Chen, K. Oh, D.Y. Pan, A facile one-step synthesis of TiO_2/graphene composites for photodegradation of methyl orange. Nano Research 4 (2011) 274–283.

15. W. Fan, Q. Lai, Q. Zhang, Y. Wang, Nanocomposites of TiO_2 and reduced graphene oxide as efficient photocatalysts for hydrogen evolution. Journal of Physical Chemistry C 115 (2011) 10694-10701.

16. M. Selim Arif Sher Shah, A. Reum Park, K. Zhang, J. Hyeok Park, P. J. Yoo, Green synthesis of biphasic TiO_2−reduced graphene oxide nanocomposites with highly enhanced photocatalytic activity, ACS Applied Materials & Interfaces, 4 (2012) 3893−3901.

LIST OF PUBLICATIONS

List of Publications in International/National Journals

1. **S. Archana,** M. Malarvizhi, P. Muthirulan and M. Meenakshi Sundaram, Superior photocatalytic and antibacterial activities of conducting ceramic TiO_2@poly(*o*-phenylenediamine) core–shell nanocomposites, ***Journal of Materials Science and Materials Electronics ,*** 1 (2016) 1-10**.**
2. **S. Archana,** M. Malarvizhi and P. Muthirulan, Simply fabricated TiO_2-graphene nanocomposites for rhodamine B dye degradation under UV irradiation towards waste water treatment applications, ***Journal of Nanoscience and Technology*** **(Accepted, 2019).**

List of papers presented in International/National conferences

1. **S. Archana,** M. Malarvizhi, P. Muthirulan, Investigation on the photocatalytic degradation performance of activated carbon supported zinc oxide on alizarin cyanine green dye under solar irradiation, ***5th International Conference on Emerging Trends in Engineering and Technology (ICETET-2018),*** Organized by Pandian Sarawathi Yadav Engineering College, Sivaganga on 9th and 10th March 2018.
2. **S. Archana,** M. Malarvizhi, P. Muthirulan, Photocatalytic degradation of rhodamine B dye using activated carbon supported TiO_2 catalyst under UV irradiation, ***National Conference on Emerging Trends in Materials Science (NCETMS-2018),*** Organized by the Department of Chemistry, Erode arts and Science College, Erode, 7th February 2018.

3. **S. Archana,** M. Malarvizhi, P. Muthirulan, Photocatalytic degradation of rhodamine B dye using graphene supported TiO_2 catalyst under solar irradiation, ***UGC sponsored National Conference on advanced materials and its applications,*** Organized by the Department of Physics, SFR College for Women, Sivakasi on 6th and 7th July, 2017**.**
4. **S. Archana,** M. Malarvizhi, P. Muthirulan, Fabrication and charecterization of TiO2-activated carbon nanocomposites for the photodegradation of safranine dye under UV radiation, 4*th* ***International Conference on Emerging Trends in Engineering and Technology (ICETET-2017),*** Organized by Pandian Sarawathi Yadav Engineering College, Sivaganga on 10th and 11th March 2017.
5. **S. Archana** participated ***'One day National Seminar on Drug addiction and De-addiction'***, organized by the Department of Chemistry, Lekshmipuram College of Arts and Science, Neyyoor on 18th February, 2017.