

MESCon 2014 [4th -5th September 2014]
National Conference on Material for Energy Storage and Conversion- 2014

Effect Of Chitosan On Photocatalytic Degradation Of Congo Red Dye Using PVC/TiO₂Nano Composites Under UV-Light Irradiation

T. Linda¹, S.Muthupoongodi², X. Sahaya Shajan²and S.Balakumar^{2*}

¹Department of chemistry, Marthandam College of Engineering,
Marthandam, Tamil Nadu, India.

²Center for Scientific and Applied Research (C-SAR), School of Basic
Engineering and Science, PSN College of Engineering and Technology,
Tirunelveli- 627 152, Tamil Nadu, India.

*Corres.author : profbalakumar@gmail.com

Abstract : In this study PVC/TiO₂ and PVC/TiO₂/Chitosan nano composites were prepared by solution cast method. Functional group of the prepared nano composites were analyzed by FTIR spectroscopy. The dispersion of chitosan in the polymer matrix was confirmed by optical microscopy. It clearly shows the chitosan in the polymer matrix. Photo decolourisation of dyes with both the systems were carried out using HEBER multi wavelength photo reactor. The photocatalytic activity was slightly increased in PVC/TiO₂/Chitosan system due to the dispersion of chitosan in the polymer matrix. Therefore the present experimental results indicate the PVC/TiO₂/Chitosan as a suitable and effective photocatalyst for the degradation of dyes.

Keywords: PVC/TiO₂ composites, photo catalytic degradation, FT-IR analysis.

Introduction

Dyes from textile and clothing industry play a crucial role in national economy. These industries produce huge amount of waste water containing harmful hazards such as carcinogenic dyes and hence create water pollution. About half of the global production of synthetic textile industry dyes are (7,000,000 tons per year) azocompounds which has chromophore in their molecular structure (-N=N-). Congo red dye (sodium salt of benzidine diazo-bis-1-naphthyl amine-4-sulphonic acid) is one of the important secondary azodye which is used for dyeing cotton in textile industry and also in paper and wood pulp industries[1]. The structure of Congo red dye was shown in the figure 1. TiO₂ it has been reported as an efficient photo-catalyst in the area of degradation due to the following properties, highly stable, non-toxic (environment or human beings), economical, complete mineralization of organic pollutants, high catalytic activity and strong oxidizing power [2,3]. Titanium dioxide is a semiconductor heterogeneous photo catalyst. Band gap is the important criteria in the choice of photo catalysts. The band gap of TiO₂ has been found to be 3.2 eV[4]. Polymer materials can be used as a support material for degradation studies. The main advantage of polymer materials is that they are chemically inert and mechanically stable with high durability [2]. Moreover the presence of hydrophobic nature

enables them to pre-concentrate the organic pollutants on the surface and this increase the efficiency of adsorption and subsequent oxidation[5].

Chitosan is eco-friendly biomaterial which possesses good chelating ability with transition metal ions. It can be used as an excellent matrix for the preparation of heterogeneous catalyst. Some of the chitosan based polymer composites were ZnO/SnO₂ chitosan film, Cu₂O- chitosan film[6]. Moreover it contains large number of reactive hydroxyl and amino group (NH₂), which exhibit excellent adsorption and chelating properties for all kinds of heavy metal ions. These properties make chitosan a suitable and excellent biomatrix for all the synthesis of efficient nanosized particles such as ZnO₂ (CdS)[7]. The literature survey indicates that the decolourisation of congo red has been worked out by many researchers over different catalysts like V/TiO₂, N, S doped TiO₂, etc. In the present study PVC/TiO₂/Chitosan nano composites thin films were prepared under mild condition. The percentage of decolourisation with different weight composition of catalyst was reported.

Experimental

TiO₂, Poly vinyl chloride (PVC), Chitosan, tetrahydrofuran were analytical grade and purchased from Merck. Millipore distillation water was used for the preparation of all solution with the resistivity of 18.2 ohm.

Certain ratio of PVC (Poly vinyl Chloride) was dissolved in tetrahydrofuran (THF) with continuous stirring to obtain the homogeneous condition. To this suspension certain ratio of TiO₂ and chitosan were added with vigorous stirring for 48hours. Then the obtained homogeneous mixture was sonicated for 1hour for the dispersion chitosan into the composites. Finally the obtained suspension was poured into petri dish and dried at room temperature. Resulting composite was dried in air oven and peeled off from the petri dish. Different weight composition of catalyst was added to 75ml of 7 ppm Congo red dye solution in a 150ml reaction vessel. At given time interval, 5ml of solution was collected to carry out the reaction.

Results and Discussion

Photo-catalytic degradation studies were carried out in HEBER multi-wavelength multilamp Photoreactor (fitted with 8w mercury lamps at 365nm, 312nm and 254 nm wavelengths). Simultaneously the degradation was noted in UV-Vis spectrometer. UV –Visible studies were carried out in Shimadzu DRS UV-2600 spectrometer. The functional group present in the composite was confirmed with the help of JASCO FTIR-4100 spectrometer.

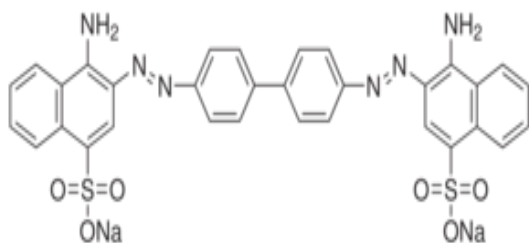


FIG. 1.The structure of Congo red dye

FTIR Analysis

FTIR spectrum was used to find the functional groups of the samples. The FTIR spectrum of PVC/TiO₂ and PVC/ TiO₂/Chitosan nano composite were analysed, and reported. The peak observed at 450-650cm⁻¹ was attributed to metal-oxide (M-O) bond. FTIR spectrum clearly shows the presence of -NH₂ and -OH group of chitosan molecule in the polymer matrix.

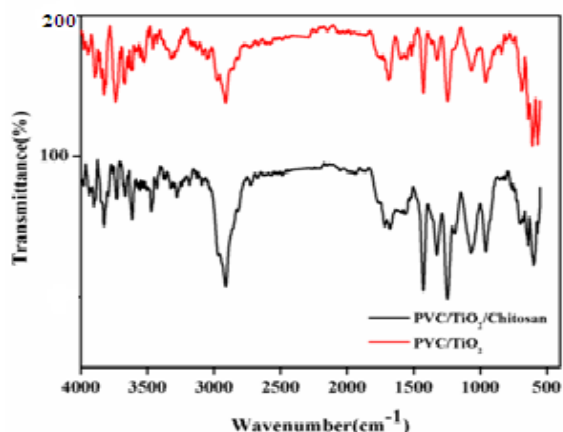


FIG.2.FTIR spectra of prepared nano composites.

Photo Catalytic Activity

The photocatalytic activities of prepared composite films were evaluated towards the decolourisation of conged red dye using HEBER multi wavelength multilamp photo reactor (fitted with 8w mercury lamps at 365nm, 312nm and 254 nm wavelengths). Simultaneously the degradation was noted in UV-Vis spectrometer. For comparison four sets of decolourisation experiments were carried out at different amount of catalyst weight. In this study we are comparing the photocatalytic activity of PVC/TiO₂ and PVC/TiO₂/Chitosan, 70 mg of the catalyst weight was used to decolorize the 7 ppm of congo red dye solution. In PVC/TiO₂ nano composite the main absorption peak was observed at 480 nm, other small peaks also observed in UV region. 80% congo red dye solution was decolorized using PVC/TiO₂ catalyst, as shown in the figure.3.

The efficiency of decolourisation was slightly increased in chitosan dispersed PVC/TiO₂, when compared to bare PVC/TiO₂. Chitosan is well dispersed in polymer matrix and the titanium can be adsorbed on the surface of chitosan, due to the coordination between Ti²⁺ and the functional groups of the chitosan (-OH, -NH₂ group). When irradiation takes place the S₂O₃²⁻ ions, which is present in chitosan are dissociated into sulfur and sulfur compounds. It is clear that the solid surface and aqueous solution form the low energy surface with heterogenic capability between the chitosan and TiO₂. Moreover the nitrogen-nitrogen double bond as the most active site, responding for oxidation is present in congo red dye. Decolourisation was noted at 15 minutes of time interval. After irradiation of 120 minutes the main absorption peak of congo red dye completely disappeared, which establish that the benzene ring and azo linkage of congo red dyes are destroyed by PVC/ TiO₂/Chitosan. Results indicate the prepared PVC/TiO₂/ Chitosan nano composite can be a suitable and effective photocatalyst for decolourisation of dye containing pollutants. The difference in the decolourisation between the two systems indicate that the not all the dye molecules are converted into mineral such as sulphates and nitrates. The larger decolourisation was obtained in PVC/TiO₂/ Chitosan nano composite, as shown in the figure 4.

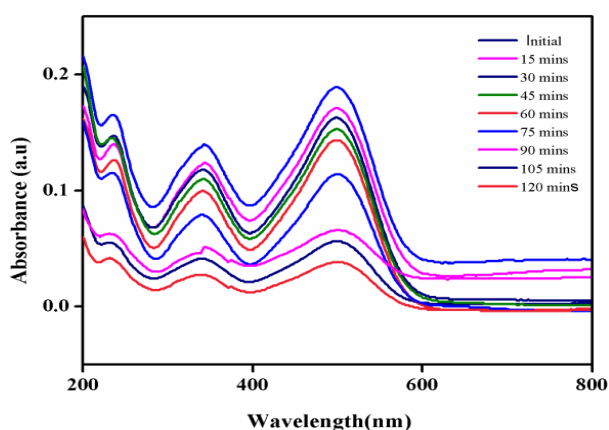


FIG.3.The decolourisation ofCongo red dye using PVC/TiO₂ catalyst

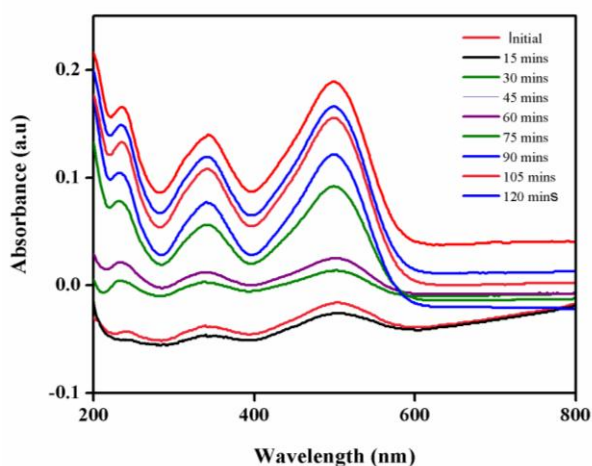


FIG.4.The decolourisation of Congo red dye using PVC/TiO₂/chitosan catalyst.

Conclusions

PVC/TiO₂ and PVC/TiO₂/Chitosan composites were successfully prepared by solution cast method. The dispersion of chitosan in the polymer matrix and the functional group of the composites were confirmed by optical and FTIR spectroscopy. The photocatalytic activity was slightly enhanced in PVC/TiO₂/Chitosan system compared to PVC/TiO₂ system. The enhancement of photocatalytic activity arises due to the presence of NH₂ and OH groups on chitosan molecules which are responsible for effective oxidation. The chitosan dispersed PVC/TiO₂ may be a promising photocatalyst material for degradation of dyes.

References

1. H. Park, W. Choi, J. Photochem. Photobiol, A 159, 241-247(2003).
2. H. Han, R. Bai, Ind.eng.Chem.Res.48, 2891-2898 (2009).
3. M. Iliva, A. Nakova, V. Tsakova, J.Appl.Electrochem.42, 121-129 (2012).
4. M. Stylidi, D.I. Kondarides, X.E. Verykios, Appl. Catal.,B 47, 189-201 (2004).
5. F. Mahalhaes, F. C. Moura, R.M, Lago, Desalination 276,266-271 (2011).
6. H. Y. Zhu, L. Xiao, R. Jiang, G.M, Zeng, L. Liu, Chem, Eng, J. 172, 746-753 (2011).
7. A. H. Chen, S. C. liu, C.Y. Chen, J .Hazard, Mater,154, 184-191 (2008).
