Facile Recoverable, Reusable and Efficient Heterogeneous Photocatalyst

Preparation and characterization of V_2O_5 added TiO_2 polymer NCs

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TiO_2 and V_2O_5 added polymer nanocomposites (NCs) were prepared by solution cast method and characterized by UV-Vis-DRS spectroscopy, powder X-ray diffraction, FTIR and SEM analysis. These characterization studies were employed to investigate the structure, optical property, phase formation and morphology of the prepared polymer NCs. The photocatalytic activities of the NCs were studied by observing the degradation of model dyes congo red (CR) and rhodamine B (RhB) under 365 nm of UV-light irradiation. In addition the recyclability and reusability of the catalyst were also examined. The results showed that nearly 95 % congo red and rhodamine B had undergone degradation in 160 and 80 min of reaction time respectively. The catalyst shows better recyclability and can be reused for at least 6 times. In particular V_2O_5 added polymer NCs shows better catalytic activity towards the degradation of organic dyes. In the photodegradation process the photo-induced holes were considered to be the dominant active species. The reported catalytic system is found to be a simple, reusable and effective model for the degradation of dye polluted effluent water.

Keywords: PVC/TiO_2, photocatalytic degradation, organic dyes, UV-Vis spectroscopy, recyclability, reusability

Long term water shortage driven by population growth and climate change are forcing people to learn to live with less water. Manufacturing industries consume a large quantity of water but until now very limited of it has been put to reuse. Recently heterogeneous photo-catalysis mediated by semiconductor TiO_2 has attracted growing attention for the purification of contaminated water and the remediation of polluted air [1, 2]. TiO_2 can be used in many applications due to its unique properties including defogging, antibacterial and anti cancer action [3]. One of the important features of TiO_2 is its ability to degrade organic pollutants such as sulforhodamine B [4], methylene blue [5], into carbon dioxide, water and inorganic salts. TiO_2 is non-toxic and chemically stable through a wide pH range [6]. However many applications are limited to UV light irradiation because the light absorption edge of titania is less than 380 nm. The structure of TiO_2 is very important for its photocatalytic activity. The key role played by the structure is extensively studied in the literature by preparing a series of compounds such as pillared TiO_2 [7, 8], TiO_2 montmorillonite nanocomposites [5], TiO_2 nanoparticles dispersed in inorganic media [9], mixed Ti/Si oxides [10] or active, non-activated carbon [11]. Among these materials, TiO_2 based composites have been reported as highly effective photocatalysts that exhibit good photocatalytic activity for the degradation of some organics in water [5, 12, 13]. The most attractive method for the synthesis of TiO_2 based nano size particles is the sol-gel process [14]. This technique does not require complicated instruments. It can provide a simple and easy way to synthesize nano size particles, which is essential for nano-photocatalysts. The advantage of the sol–gel method is that it can effectively control the microstructure [15] and chemical properties of titania nano size particles by varying the titanium precursor, the solvent, acidic or basic additives, the synthesis and calcinations condition [16, 17]. Recently, vanadia-doped titanium-pillared clay showed excellent activity in the epoxidation of allylic alcohol (E)-2-hexen-1-ol [18], the selective catalytic oxidation of H_2S [19] and the selective catalytic reduction (SCR) of NO by NH_3 [20]. A study on the photodegradation of dyes under UV light by TiO_2-based polymer NCs as catalysts has been reported here. Consequently the quantum efficiency of TiO_2 catalysts in solar energy utilization application is low. It is desirable to have a red shift in its response spectrum, which may be achieved by (doping or co-doping) of TiO_2 with oxides of metal elements such as V, Fe, W, Cr, Mo, Nb, Zn, Sn, Zr or nonmetallic elements such as B, N, S and C. Reducing the optical band gap may enhance the visible light absorption but at the same time it may enhance the electron hole recombination [21]. This calls for development of photocatalyst, which shows visible light response as well as the decreased charge carriers' recombination. The charge carrier recombination may be reduced by separation of electrons and holes using noble metal electron scavengers like silver and platinum [22]. Recently V doped TiO_2 has been reported by Kubacka et al. to show higher absorption in the red shifted spectrum compared to the oxides of N, W and Mo. Pentavalent V oxides are expected to make a net contribution in photo generation of holes because V has high charge to volume ratio compared to Ti. Also high relative polarizability of V makes transfer of photogenerated electrons easier as well as the scavenging of electrons more probable, thereby increasing the average life time of holes.

However the low solubility of V in anatase structure (about 5 %) limits its performance potential. Also a red shift in the absorption spectrum does not ensure a proportional increase in the photocatalytic activity, due to carrier recombination.

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In the present work, the polymer NCs of PVC/TiO_2 (PVC/T) and PVC/TiO_2/V_2O_5 (PVC/T/V) are prepared to function as UV light response catalysts. The effect of washing medium on photodegradation efficiencies of dye in the preparation process is studied. The photocatalytic efficiency of the prepared polymer NCs are evaluated by degradation of congo red (CR) and rhodamine B (RhB) as model dyes. PVC/T/V polymer NCs are found to be more efficient in dye removal and suitable for practical applications in water purification technologies.

Experimental part

The chemical substances used for synthesis were all 99 % + pure (Merck): Titaniumbutaoxide (TBO), ammonium meta-vanadate (NH_4VO_3), sodium hydroxide (NaOH), poly vinyl chloride (PVC), congo red and rhodamine B dye. Demineralized water (with a resistivity of 18.2 MN) was used throughout the study. The other solvents tetrahydrofuran (THF) and ethanol used were distilled in vacuum and kept dry (99 % pure).

Synthesis of TiO_2 nanoparticles

Titanium dioxide nanoparticles used in this study were synthesized via sol gel method from TBO. A 1:1 mixture of water and ethanol was first stirred for 30 min at room temperature. The pH of the solution was maintained with hydrochloric acid and stirred well for an additional 30 min. TBO was mixed with an equal volume of ethanol and added drop wise into the ethanol/water mixture. After the addition of TBO the mixture was stirred for 3 h at room temperature. Then the solution was refluxed at 80ºC for 18 h to condense into TiO_2. The resulting gel was centrifuged to remove excess water and ethanol, dried at 500ºC in air oven for 5 h to remove any remaining precursors of butanol, ground well for 120 min. Thus synthesized TiO_2 nanoparticles were used for further studies.

Preparation of polymer NCs

The preparation of polymer NCs was reported [23]. The prepared polymer NCs is shown in (fig. 1). The prepared polymer NCs here after called as PVC/TiO_2→PVC/T and PVC/TiO_2/V_2O_5→PVC/T/V.

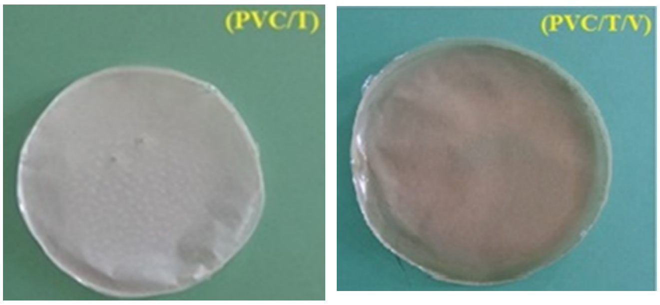


Fig. 1. Photograph of PVC/T and PVC/T/V polymer NCs

Characterization

The energy dispersive X-ray (EDX) analysis of nano particles was carried out in sophisticated instrument facility, Cochin, Kerala, India. The diffused reflectance UV-visible (DRS-UV-Vis) spectra were recorded with the help of Shimadzu-2600 spectrometer with spectral range of 220-1200 nm (for the absorbance of synthesized metal oxide nanoparticles) and 200-800nm (for the measurements of dye absorbance during catalytic degradation studies). The sample cell (Quartz) of appropriate size and 1 cm path length was used. It was placed directly in the sample holder. Fourier transform infrared (FTIR) spectrum was recorded using a JASCO FTIR 4600 spectrometer in the wave number region 400-4000 cm^{-1}. SEM analysis was carried out using (JEOL Model JSM – 6390 LV) with the magnification range of 5 × 300,000. The powder X-ray diffraction patterns of the synthesized nanoparticles were taken using a Philips X'pert Pro diffractometer (operating at 40 kV and 30 mA) with CuKá radiation (λ= 1.5418 Å) scanned over the 2θ range of 10-80° at the rate of 2°/min.

The photocatalytic degradation studies were carried out using HEBER multilamp photo reactor. 24 numbers of low pressure mercury vapor lamps (Sankyodenki, Japan) of 8W emitting wavelength at 365 nm along with metallic specially coated holders with proper heat resistant insulation are provided.

Results and discussions

Energy dispersive X-ray analysis (EDAX)

The results obtained through energy dispersive X-ray analysis confirms the presence of TiO_2 (Ti and O_2). The elemental composition of the TiO_2 was found to be 47.4 % of Ti and 52.6 % of O by which the presence of elements Ti and O was confirmed. The energy dispersive spectra are given in the (fig.2).

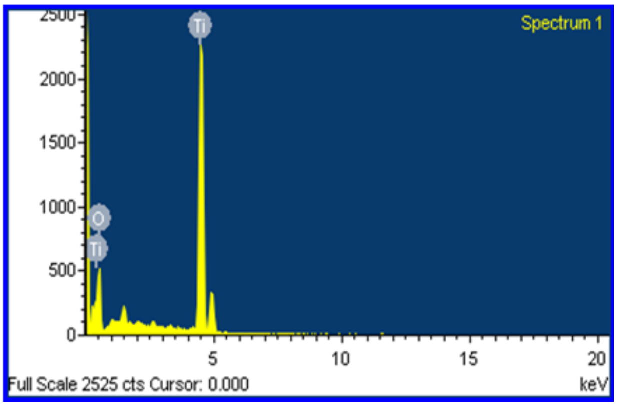


Fig. 2. Energy dispersive X-ray spectra of TiO_2 nanoparticle

Powder X-ray diffraction analysis

The powder X-ray diffraction pattern of TiO_2 and its composites is given in the (fig.3).

The powder X-ray diffraction analysis is performed to know the phase formation of synthesized TiO_2 nanoparticles. The wide angle powder X-ray diffraction

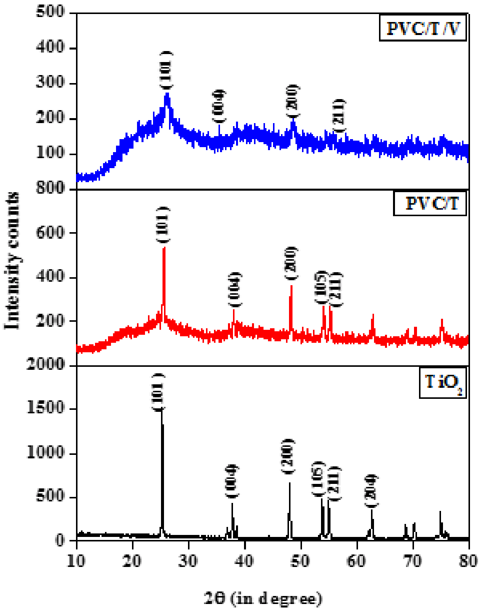


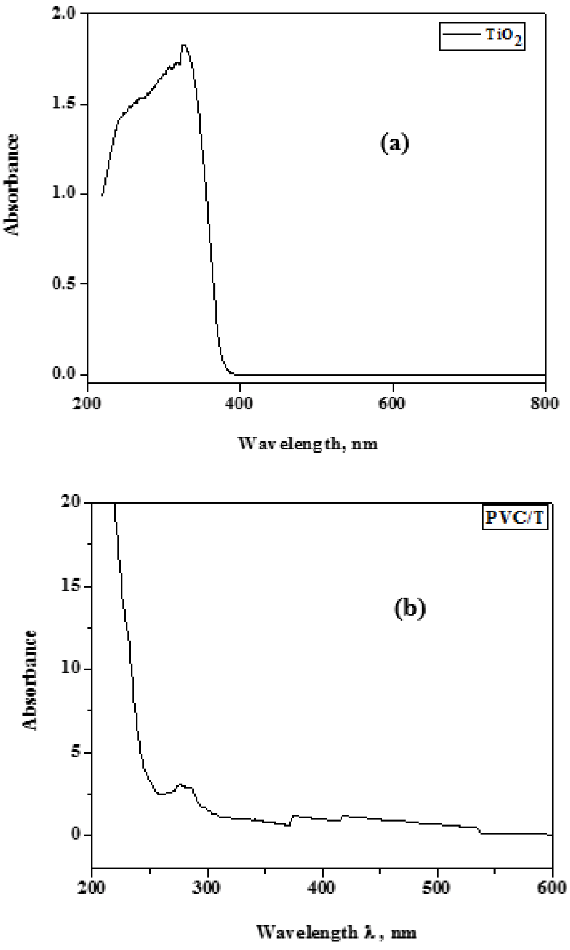
Fig. 3. Powder X-ray diffraction pattern of TiO_2, PVC/T and PVC/T/V polymer NC

was recorded over the 2θ range of 10 - 80°. The lattice constant values of the tetragonal phase of the TiO_2 nanoparticle is a = 3.785 and c = 9.513. This is in good agreement with the standard JCPDS data (JCPDS card No.21-1272).

Figure 4a shows the strong and sharp peaks analogous to the tetragonal structure of TiO_2 nanoparticles. The characterization peaks observed in the 2θ range at 25.2°, 39.7°, 48.1°, 53.8°, 55.0° and 62.7° can be attributed to the (101), (004), (200), (105), (211) and (204) and plane of the tetragonal structure of TiO_2 nano particles. The TiO_2 has 2θ range of 25.1° in its tetragonal phase in PVC/T and PVC/T/V polymer NCs. In the PVC/T/V polymer composites this value has been slightly shifted to 26.3° due to the incorporation of the metal oxide V_2O_5. In the case of PVC/T/V the additional peak is noticed in the 2θ range of 26° and 74° corresponding to V_2O_5. The introduction of V_2O_5 in the polymer matrix does not alter the tetragonal form of the crystal as shown in the (fig. 3). The crystallite size was calculated using Debye-Sherrer formula [24]. The calculated crystallite size of the TiO_2, PVC/T and PVC/T/V NCs are 81.0, 40.5 and 10.1 nm respectively. The crystallite size decreases with the incorporation of V_2O_5.

Ultra violet spectroscopy

The UV-Vis spectra of TiO_2 and polymer NCs were presented in (fig. 4a, b, c). The UV-Vis absorption of TiO_2 nano particles was measured in the wavelength range of 220 -1200 nm. The maximum absorption is found to be in 380 nm and small absorption observed around at 280 nm. In PVC/T and PVC/T/V composites contain TiO_2 nanoparticles and this has been observed by the strong absorption band at 280 nm. This peak arises due to the transfer of electron from valance band to conduction band of TiO_2 nanoparticles. The figure PVC/T/V representing the slight absorption of the polymer composites containing mixed oxides shows an absorption peak in the region 300-390 nm due to the presence of V=O group. The UV spectrum of all the composites gives an idea about the components present in the polymer composite and uniform dispersion of oxides on the polymer matrix. From the UV-visible spectra it is possible to calculate the energy of the



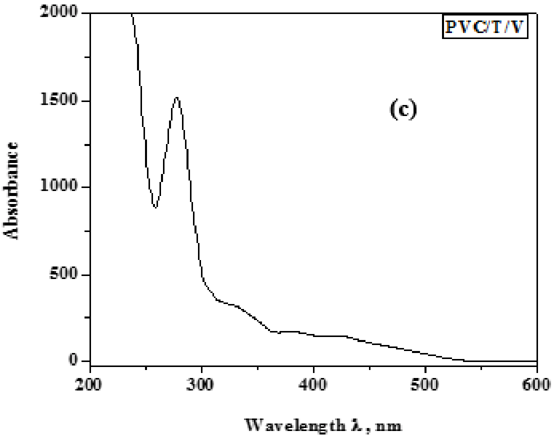


Fig. 4. UV-Vis-absorption spectrum of TiO_2, PVC/T and PVC/T/V polymer NCs

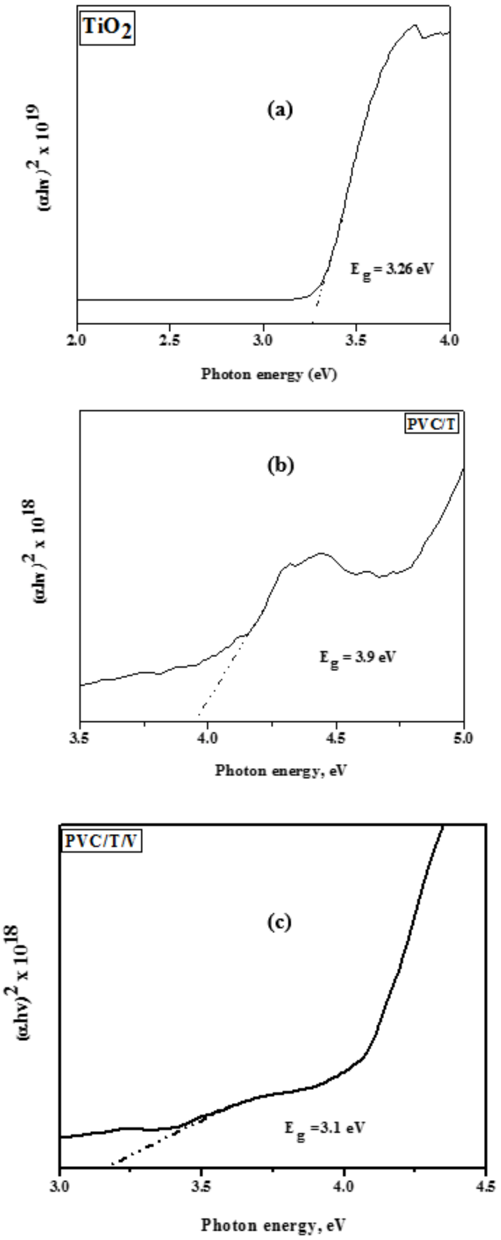


Fig. 5. Taucs plot of TiO_2(a), PVC/T(b) and PVC/T/V(c) polymer NCs

band gap created by the semiconductor metal oxides dispersed in the polymer matrix. For this purpose Kubelka-Munk [25] equation along with Taucs plot is used (fig. 5). Taucs plot refers to the plot of $h\nu$ Vs ($\alpha h\nu$)1/2 of the polymer composites. The calculated band gap energy values are, 3.26, 3.9 and 3.1 eV for, TiO_2, PVC/T and PVC/T/V respectively.

Fourier transform infrared spectroscopy

FTIR spectrum of TiO_2 nanoparticle and polymer NCs is given in the (fig.6).

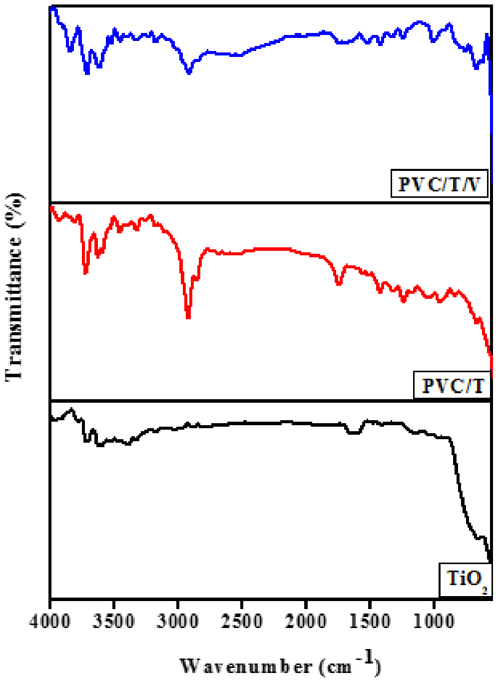


Fig. 6. FTIR spectrum of TiO_2 nanoparticle, PVC/T and PVC/T/V polymer NCs

The peaks observed at 3400 and 1613 cm^{-1} are due to the stretching and bending vibrations of -OH group [26]. The peaks at 700 cm^{-1} , show the stretching vibration mode of Ti-O. There is no peak at 2900 cm^{-1}, which means that all organic compounds are removed from the samples. From the (fig.6) it is noticed that the two composites (PVC/T and PVC/T/V) have similar characteristic peaks TiO_2. There is a band at 2914 cm^{-1} corresponding to-CH stretching of polymer PVC and another band at 700 cm^{-1} due to metal oxygen (Ti-O) bond in PVC/T and PVC/T/V polymer nanocomposites. The -OH stretching vibration of water molecules found at 3500 - 3700 cm^{-1} confirms the presence of water molecules in the composites and the band appearing in the wavenumber region 1699 cm^{-1} is associated with the bending vibration of water molecules. The stretching vibration at 2923 cm^{-1} is due to the residual organic component ethanol left during washing. The study of IR spectra confirms the presence of all the components in the polymer nanocomposites.

Scanning electron microscopy

Figure 7a shows the SEM image of the TiO_2 nano particles.

It shows that the synthesized TiO_2 nano particles are well dispersed throughout and agglomerated in some places. Moreover, the surface has many irregular small granules with spongy shape. Figure 7b & c shows the SEM image of the PVC/T and PVC/T/V polymer NCs. TiO_2 is distributed in the two polymer NCs. The relative study of PVC/T/V and PVC/T NCs shows the presence of fine granules on the surface without aggregation in PVC/T/V and with agglomeration in PVC/T NCs. The study of SEM images further lends credence to the results of XRD studies.

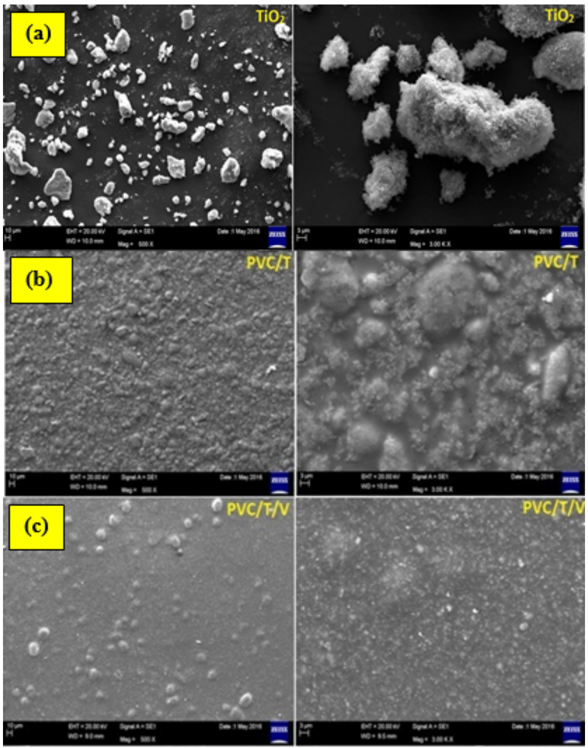


Fig. 7. SEM images of TiO_2 nanoparticle (a), PVC/T (b) and PVC/T/V (c) polymer NCs

Description of photo degradation process

The degradation studies were carried out using suitable photocatalyst in the photo reactor. The organic dyes used for study are congo red (CR) and rhodamine B (RhB). The three polymers nano composites synthesized were used as photocatalyst independently in each study. The reaction mixture is subjected to UV radiation at 365 nm. A known concentration of CR and RhB organic dyes (7 ppm in 75 mL) is taken in the reaction vessel. Certain (10, 30, 50 and 70 mg) weight of catalyst was added into the reaction vessel. The λmax for congo red is observed at 490, 348 and 238 nm and rhodamine B at 553 nm. The organic dyes were subjected to radiation (365 nm) for a definite period of time. UV spectrum is recorded periodically with samples withdrawn from reaction vessel. The radiation is continued till 95 % degradation is obtained. The spectrum is recorded and the result is discussed herein.

Photocatalytic activity

For the degradation of CR dye 7 ppm of its concentration was used throughout for different amounts of (10, 30, 50 and 70 mg) catalyst loading as a function of time. The CR solution has an absorption band at 490 nm in the visible region and 238, 348 nm in the UV region respectively. The photocatalyst is added to the CR solution and then exposed to UV irradiation. Degradation sets in and the process of degradation is shown in the (fig. 8) corresponding to each catalyst.

It has been found that the amount of catalyst added strongly influences the photocatalytic reaction. As the reaction progresses, the increase in the catalyst load increases photodegradation at first, however excess of catalyst added has no effect later on and the optimum concentration of the catalyst has been determined to ensure efficient process. Above the optimum concentration there is light scattering and screening effect

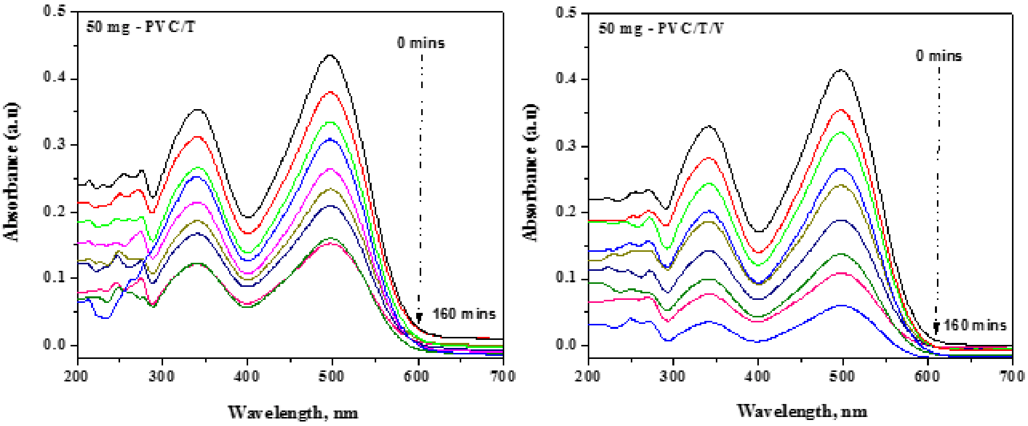


Fig. 8. Photodegradation of CR dye solution using PVC/T and PVC/T/V polymer NCs

which reduce the specific activity of the catalyst. Under these conditions the catalytic surface probably becomes no more available for absorption of photons and hence no more stimulation for photocatalytic reaction. 50 mg of the photocatalyst has been found to be the optimum concentration for all the catalysts. The cursory view of (fig.8) shows that there are three peaks at 490, 238 and 348 nm corresponding to the azo group, benzene and naphthalene respectively. The intensities of all the three peaks progressively decrease with time and reach a minimum after a period of 160 mins of irradiation. In the case of azo group, degradation is fast due to lower bond energy. Benzene ring being more stable than the naphthalene ring it disappears slowly in the degradation process. Thus the degradation initially occurs at the low energy bond of azo group proceeding towards the high energy benzene ring in the last. The degradation process is complete in CR dye with the disappearance of its benzene, naphthalene and azo groups. Among the two photocatalysts PVC/T/V polymer nanocomposites shows greater photocatalytic activity than PVC/T during a period of 160 min. This phenomenon may be due to that the wavelength range of V_2O_5 added TiO_2 composite is extended to the visible region. The excitation of 3d electron from vanadium (V_2+5) center to the TiO_2 conduction band is caused by UV absorption. The photo-excited electron enables chemical reactions to occur on the surface of the V_2O_5 added catalyst under UV light radiation, because normally the oxidation of V4+ to V5+ occurs at 2.1 eV [27] which is below the TiO_2 conduction band and V_2O_5 added TiO_2 catalyst can absorb light between 2.7 eV and 2.5 eV [28, 29].

For the degradation of RhB dye maximum absorption peak intensity is observed at 553 nm. This absorption peak intensity gradually decreases upon UV irradiation in the presence of catalyst and nearly disappears after 80 mins. There is complete disappearance of the peak when PVC/T/V nanocomposites are involved. The results show that (fig. 9) in general the nanocomposites have great photodegradation efficiency, with PVC/T/V composite comparatively more efficient than PVC/T.

The result of experiments conducted with different amount of catalyst for CR and RhB dye is given in the (fig. 10 and 11).

The C/Co [where C is the main absorption peak intensity of (CR & RhB) dye at each irradiation of time interval at a wavelength of 365 nm and Co was the initial absorption peak intensity of 7 ppm (CR & RhB) solution]. In the case of PVC/T polymer NCs the degradation is only 79 of RhB, while 97 % of the same is degraded by PVC/T/V in the same period of 80 min. For CR dye degradation 65 and 95% efficiency was obtained for PVC/T, PVC/T/V

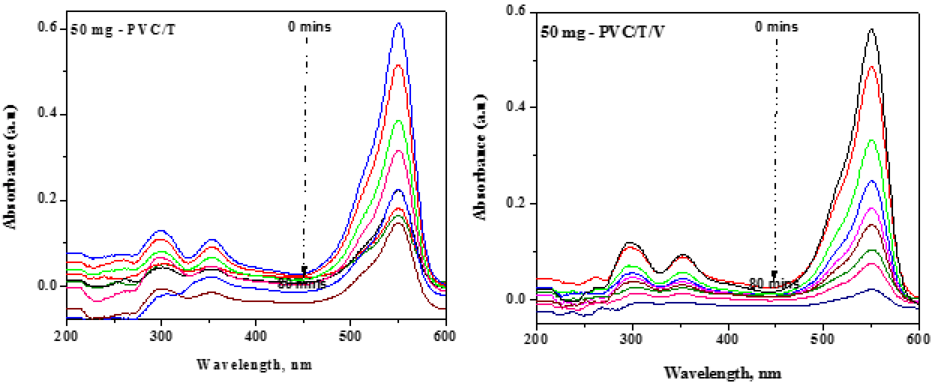


Fig. 9. Photodegradation of RhB dye solution using PVC/T and PVC/T/V polymer NCs

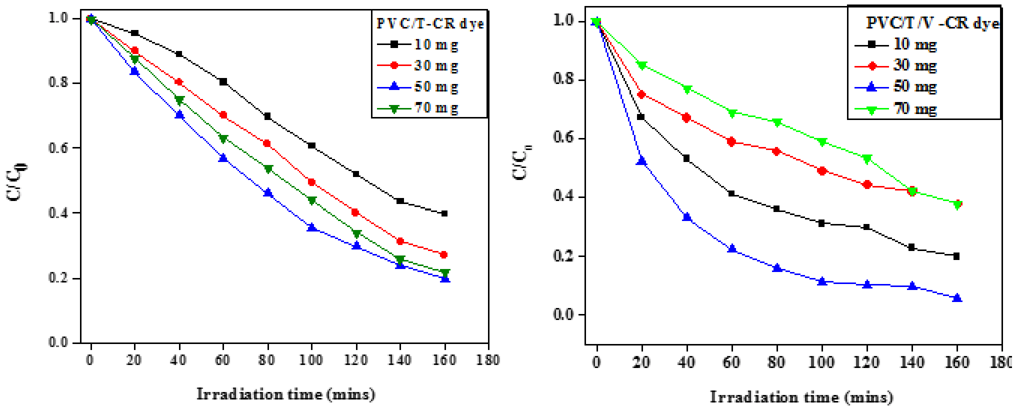


Fig. 10. Photodegradation of CR dye solution with different dosage of PVC/T and PVC/T/V polymer NCs

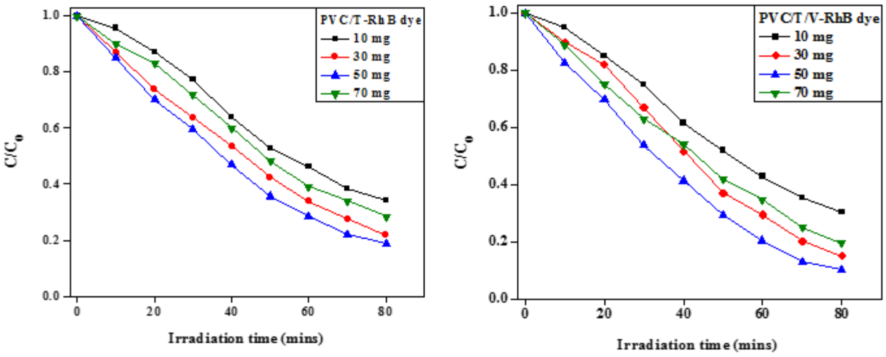


Fig. 11. Photodegradation of RhB dye solution with different dosage of PVC/T and PVC/T/V polymer NCs

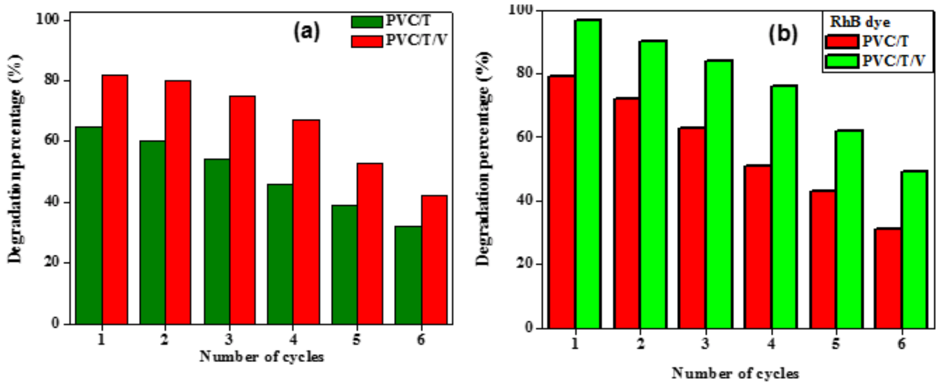


Fig. 12. Stability and reusability of polymer NCs at 7ppm in CR (a) and RhB (b) dye solution

respectively. Thus PVC/T/V nanocomposites act as a better catalyst compared to the PVC/T. This is true for both the CR and RhB dyes. The photocatalytic activity on V_2O_5 added TiO_2 composite is faster than that on PVC/T composite. Based on the above results, a proposed mechanism was being discussed to explain the enhancement of the photocatalytic properties of the PVC/T/V composite which was similar to the literature [30, 31]. The mechanism was that the high photocatalytic activity of the V_2O_5 added TiO_2 composite was mainly attributed to the bridge effect of PVC in facilitating the separation efficiency of electrons and holes. Under UV light irradiation, both TiO_2 and V_2O_5 absorbed the photons. The high energy photon excites an electron from the valance band (VB) to the conduction band (CB) of TiO_2 and V_2O_5. Because the CB levels of TiO_2 and V_2O_5 are located significantly higher than the Fermi level, photogenerated electrons in TiO_2 and V_2O_5 would move freely to the surface of PVC. At the same time, the photo-generated holes were left in the VB of TiO_2 and V_2O_5. The holes were ultimately trapped by surface hydroxyl groups at the catalyst surface to yield $OH^{\cdot}$ radicals, which was a strong oxidizing agent to decompose the organic dye. The dissolved oxygen molecules reacted with the surface electrons to yield superoxide radicals anion $O_2^{\cdot-}$, which on protonation generated the hydroperoxy, $HO_2^{\cdot}$, radicals, producing hydroxyl radical $OH^{\cdot}$. The efficient charge separation could increase the lifetime of the charge carriers and enhance the efficiency of the interfacial charge transfer to absorbed substrates and then account for the higher activity of the V_2O_5 added TiO_2 composites.

Stability and reusability of the catalyst

The stability and reusability of the photocatalyst is an important parameter for the photodegradation process. To examine the stability and reusability, recycling experiments are carried out for all the three photocatalysts. The results are presented in (fig. 12 a & b).

For each new cycle, the photocatalyst is reused for the decolorization of organic dye solution under similar conditions. The photocatalysts were washed with ethanol/water and dried before reused. The results indicate that after the 5th cycle the decolorization percentage of CR dye is 32, 46 and 31, 49 of RhB dye for PVC/T, PVC/T/V NCs respectively. The photocatalytic activity of PVC/T NCs was very low for the decolorization of CR and RhB dye when used at 6th cycle. However, the PVC/T/Vs photocatalysts show relatively good decolorization percentage of CR and RhB dyes even in the 6th cycle. There is general decrease in catalytic activity after second use and after wards the catalysts are relatively stabilized.

Conclusions

TiO_2 and V_2O_5 added polymer NCs are prepared and well characterized by different techniques. They are further employed for degradation studies of organic dyes. The experiment results indicate V_2O_5 added TiO_2 polymer NCs have relatively higher photocatalytic activities than PVC/TiO_2 catalyst. Both the catalyst are stable, however their photocatalytic efficiency is different though all of them can be reused for a number of times. PVC/T/V exhibits greater photocatalytic activity and PVC/T shows minimum activity during the fixed time interval of irradiation. According to the mechanism for photocatalytic reaction the significant photocatalytic activity may be due to lower recombination of e- - h+ and extended life span of e- - h+ pairs. Besides, the high activity of V_2O_5 added TiO_2 NCs can be due to its smaller particle size, its relatively larger surface area and the blue shift of the on set absorption edge in the UV–Visible DRS. However, the high activity of V_2O_5 added TiO_2 can be ascribed to the significant photoabsorption in the UV region and Ti active sites of the partial pillared nanocomposites which are easier to touch with dye and lead to a higher degradation rate.

Acknowledgement: The authors (S.Muthupoongodi & T. Linda) gratefully acknowledge the PSN College of Engineering & Technology, for giving research facility.

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Manuscript received: 24.05. 2017