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Photoactive TiO_2/polyamide 11 (TiO_2/PA-11) nanocomposite for degradation of methylene blue dye in wastewater

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Abstract

Photocatalytic degradation of methylene blue dye (MB) was in aqueous solution using untreated titanium dioxide nanoparticles (TiO_2 NPs) and TiO_2/polyamide 11 (TiO_2/PA-11) under visible light irradiation. The effects of catalyst loading and pH values on the dye degradation were studied. An aqueous solution of MB was degraded by more than 95% with TiO2/PA-11 (200 ppm) after visible light irradiation at 360 min. However MB dye was degraded by more than 99% for 180 min with TiO2/PA-11 at pH 10.

Keywords: Polyamide-11/TiO_2 nanocomposite; Photocatalyst, Photodegradation, Methylene blue dye, Water treatment.

1. Introduction

The release of dye in textile effluents into the ecosystem is a substantial source of non-aesthetic pollution, eutrophication, and perturbation in aquatic life [1]. The photocatalytic degradation of methylene blue (MB) was chosen as a model reaction in many reports because this dye is a typical conjugated aromatic dye, to evaluate photocatalyst activities due to the obvious change to blue during photocatalytic degradation [2-4]. Recently, the use of polymer hybridized with nanomaterials to be used as photoactive material in wastewater treatment process has attracted a great attention from eco-friendly point of view [5,6]. The design of a conjugated photoactive materials and its incorporation into a series of polymers have been attracted attentions. Hence, the need for development of more sustainable catalytic systems is on-going. Hybridization of TiO_2 nanoparticles (NPs) with polymeric materials could impede the recombination of excitons (electron–hole pairs) [7-9] and the barrier at the TiO2 interface can separate the photoinduced electrons and holes effectively, which leads to enhancing the photocatalytic activities [9]. Polyamide 11 with zero band-gap energy [10,11], as a result the surface modification of TiO_2 with PA-11 can improve the photocatalytic performance of TiO_2 photocatalysts, in comparison with pure PA-11 or TiO_2 NPs. TiO_2 showed activity in the ultraviolet region (ca ~ <400 nm), which represents <10% of the overall solar intensity. Therefore, the light harvesting ability of TiO_2 is very limited [12]. The photocatalytic activity of TiO_2 has some limitations such as the wide energy gap (ca ~ 3.2 eV) that minimize its application to UV region and the fast recombination of charge carriers [13]. The main challenge in this field is to design an efficient TiO2 based photocatalyst, which is working efficiently under the visible light region [14-20]. The present work aims to study photocatalytic degradation of MB in the presence of modified titanium dioxide nanoparticles (TiO_2 NPs) conjugated with polyamide 11 (PA-11) with low energy band gap that can utilize visible light in the degradation process. The effect of operational conditions such as catalyst dose, and pH on the degradation efficiency of MB was demonstrated. Characterization of the dye degradation intermediates was carried out using High resolution mass spectroscopy that gave a pattern of the methylene blue dye degradation pathway. **2.**

Experimental:

General

Titanium dioxide nanopowder was purchased from Sigma-Aldrich company and having the specific

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surface area (35-65 m^2/g). In addition, polyamide 11 and ethanol were also purchased from supplier and were used without further purification. Phase and crystallinity were investigated by X-ray diffraction (XRD) analysis using a Philips PW1710 X-ray diffractometer using Cu Ka radiation (k = 1.54186 A˚) employing Cu-Kα radiation (λ = 1.54 Å) operated at 30 mA and 40 kV. The morphology, purity, and elemental composition of the samples were characterized using a scanning electron microscope (SEM) supported with energy-dispersive X-ray spectroscopy (EDX) unit with a Philips CM20 microscope, operating at an accelerating voltage of 200 kV. The intermediates of methylene blue degredation were evaluated LC/TOF-MS (Agilent 6230 time-of-flight LC/MS (LC/TOF).

Preparation of TiO_2/PA-11 nanocomposite

PA-11 (1.0 g) was dissolved in 50 mL of ethanol. To this solution, 0.1 g TiO_2 NPs dissolved in 50 mL of H_2O were added under vigorous stirring and the stirring was continued for 60 min. Then, treated the mixture at 105 ºC to achieve the deposition of TiO2 for 60 min, then the precipitate was filtered, washed with ethanol and deionized water (30 mLx5 times). Finally, the resultant composite was dried at 50 ºC in vacuum for 3 h.

Photodegradation of Methylene Blue

The TiO_2 and TiO_2/PA-11 samples (5, 10 or 20 mg) of were loaded with 100 mL of MB solution (10μM) in cylindrical quartz vessels. The suspension was irradiated with light emitting diode (LED) lamp (LED bulb, Canyon, 20 Watt, λ = 400-750 nm) for photodegradation under stirring. The temperature was kept constant at 25 ºC all the experiments to avoid the thermal degradation.

3. Results and Discussion:

Scanning electron microscope analysis

SEM analysis with magnification 100000x was performed for TiO_2 and TiO_2/PA-11 samples. That was detected the particles size within range 9.28-20.12 nm for TiO_2 and 12.5-27.32 nm for TiO_2/PA-11, respectively (Fig. 1a,c).

The elemental composition of the nanocomposites is calculated from the EDX spectra (Fig. 1b,d). The obtained EDX spectrum for TiO2 NPs confirmed the presence of Ti and O with 59.89 wt%, 40.11 wt%. In case of TiO_2/PA-11 composite, the determined values for C, N, Ti and O are 53.41 wt%, 4.77 wt%, 16.39 wt%, 16.43 wt%, respectively. From the results, it was demonstrated that the polyamide 11 scaffold can be bonded to TiO_2 NPs. Scheme 1 illustrated the possible structure of the TiO_2/PA-11 nanocomposite according to previously reported studies [7,8].

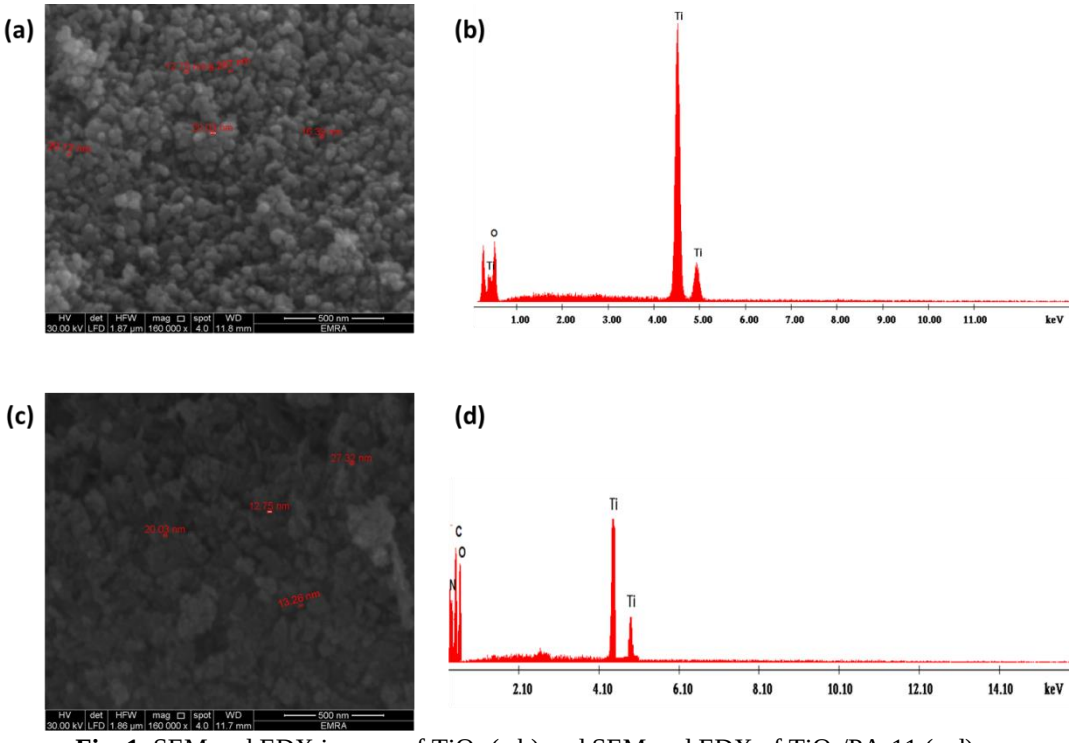
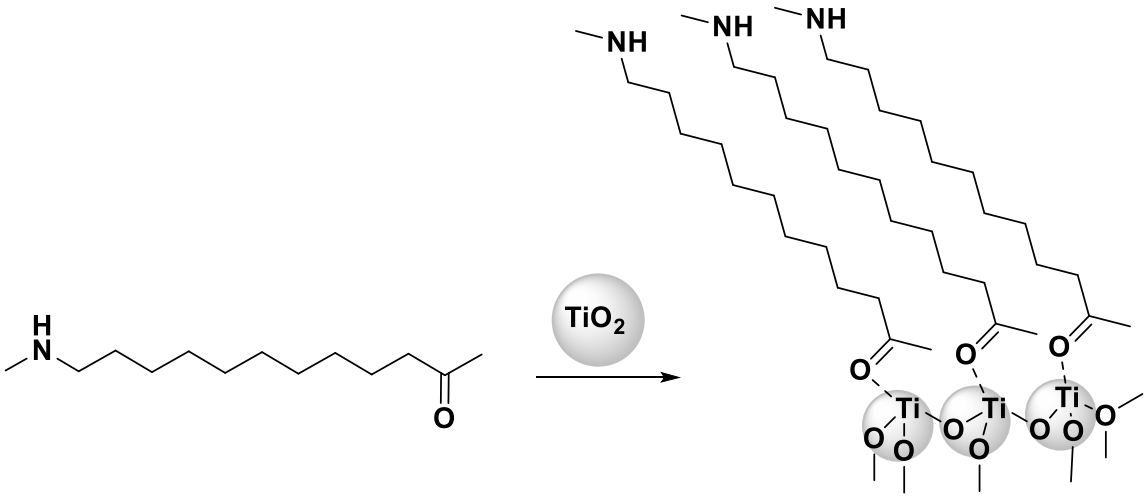


Fig. 1. SEM and EDX images of TiO_2 (a,b) and SEM and EDX of TiO_2/PA-11 (c,d).



Scheme 1. Formation of TiO_2/PA-11.

X-ray diffraction (XRD) analysis

The XRD patterns corresponding to TiO_2 and TiO2/polyamide 11 were observed in (Fig. 2) in which a confirmation on the formation of the as prepared nanocomposites with a single phase anatase structure without detecting any secondary phase had been investigated.

For anatase TiO_2 and TiO_2/PA-11, it was depicted that the lines are located at 2θ angles of 27.51º, 31.87º, 45.57º and 64.59º corresponding to (210), (113), (124), and (220), respectively, [21].

The UV-Vis analysis

The UV-Vis-Diffuse reflectance spectra (DRS) for TiO_2 and TiO_2/PA-11 were determined in the range of 300-800 nm (Fig. 3). The bandgap of the samples was calculated by the equation (Eg =1239.8/λ) [22], where Eg is the bandgap energy (eV) and λ (nm) the wavelength of absorption edges in the spectra. Thus, the bandgap of TiO_2 was found 3.25 eV, while for TiO_2/PA-11 is 2.70 eV.

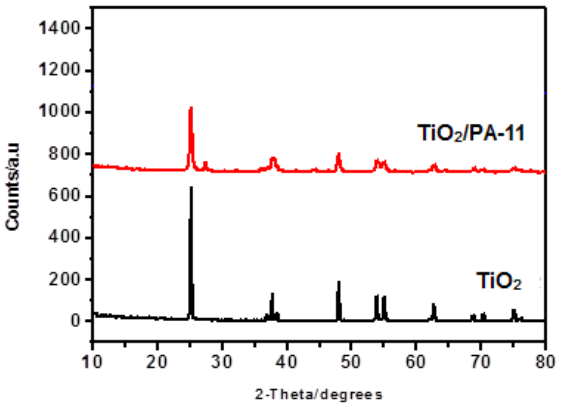


Fig. 2. XRD of TiO_2 (a), TiO_2/PA-11.

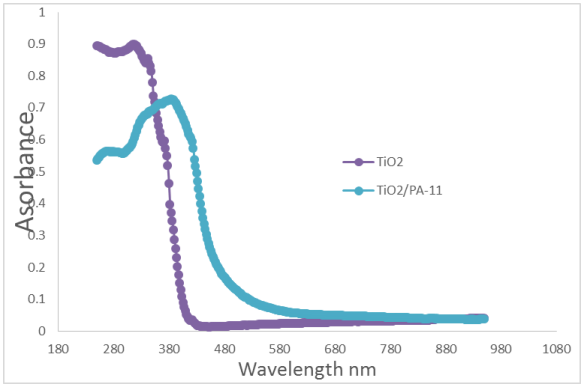


Fig. 3. UV-Visible absorption spectra, (a) TiO_2 and (b) TiO_2/PA-11.

Photocatalytic activity towards degradation of methylene blue (MB) dye

The photocatalytic performance of TiO_2 and TiO_2/PA-11 were determined by degradation of methylene blue dye (MB) in aqueous solution under visible light irradiation. The photodegradation was monitored by measuring UV-Visible absorption spectra.

Effect of catalyst loading

The effect of catalyst loading for degradation of Methylene Blue (MB) at ambient condition was investigated. It was found that the untreated TiO_2 nanoparticles showed no catalytic activity towards the degradation of dye under visible light irradiation. However when TiO_2/PA-11 nanocomposite (50, 100 or 200 ppm) was added to a solution of MB dye with stirring at pH 7 for 6 h at 25 ºC, it was found that by using the catalyst (200 ppm) the degradation of MB was completed with more than 95% under visible light irradiation (Fig. 4). It was indicated that as the weight of the catalyst increased, as the degradation of dye proceed efficiently, that might be resulting from the higher surface area exposure

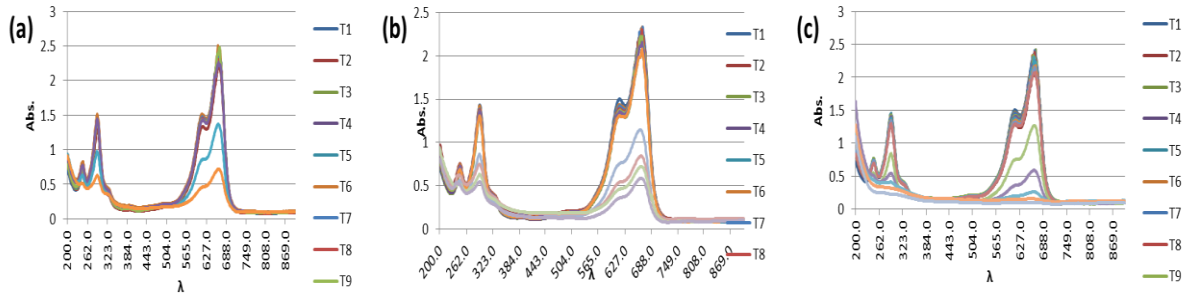


Fig. 4. The effect of catalyst loading at pH 7, 5mg (a), 10 mg (b), 20 mg (c).

Effect of pH

The pH effect on degradation of MB was studied. The proficiency of TiO_2/PA-11 catalyst (200 ppm) was tested under acidic condition at pH 2 and at basic condition at pH 10. It was revealed that at acidic condition for 36 h, the MB dye was not fully degraded (Fig. 5a). However, at pH10, the dye was degraded after 2 h. As shown in figure 5, it was indicated that the rate of dye degradation was increased under basic condition and the dye was degraded with more than 99% (Fig. 5b).

The mechanisms of photodegradation of MB by TiO_2/PA-11

Using LC-TOF-MS, the intermediate products of MB degradation were identified. Heterogeneous photocatalysis is sustainable advanced oxidation process (AOP) for the removal of organic pollutant. photodegradation process, MB molecules readily adsorb onto the PA-11 surface and such strong adsorption should facilitate the transfer of electrons between dye molecules and TiO_2. We identified various intermediate products, including adduct A (m/z = 270), adduct B (m/z = 256), adduct C (m/z = 228), that were formed via demethylation cleavage during the photocatalytic degradation, and phenol (m/z = 94) (Scheme 2 and Fig. 6).

Two main key factors in the photocatalytic activity were solar absorption and charge separation. In the primary reaction process, TiO_2 is excited under light irradiation to generate electron–hole pairs. In the secondary reaction process, reactive oxygen species (ROS) are produced to degrade the organic pollutant [23,24]. Therefore, the TiO_2/PA-11 is a photosensitizer, based on its narrow band gap, PA-11 modified TiO_2 inserts the energy level of PA-11 into the energy level of TiO_2, enhancing its visible light sensitivity. Therefore, the mechanism for enhanced photocatalytic activity is based on photosensitization. When the photoreaction between MB solution with TiO_2/PA-11 was irradiated under light, photoinduced electrons and holes are formed due to the excitation of TiO_2.

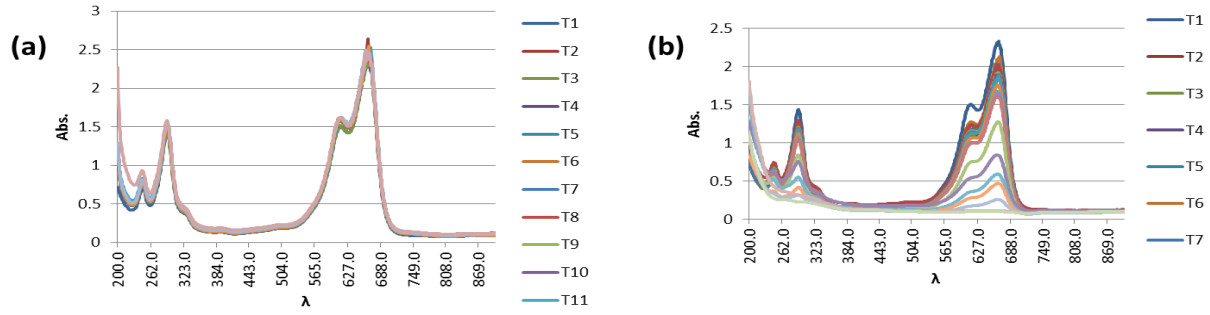
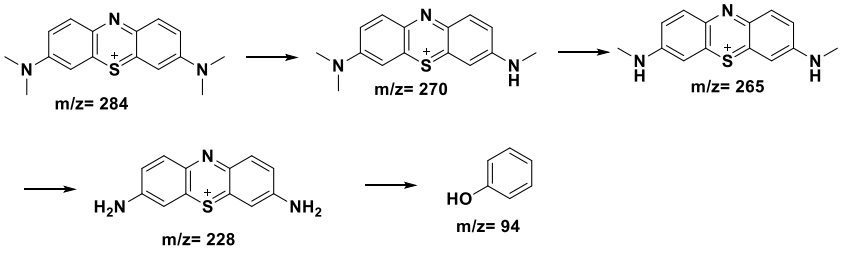


Fig. 5. The effect of pH value at concentration of catalyst = 200 ppm, pH 2 (a), pH 10 (b).



Scheme 2. Degradation of the MB dye.

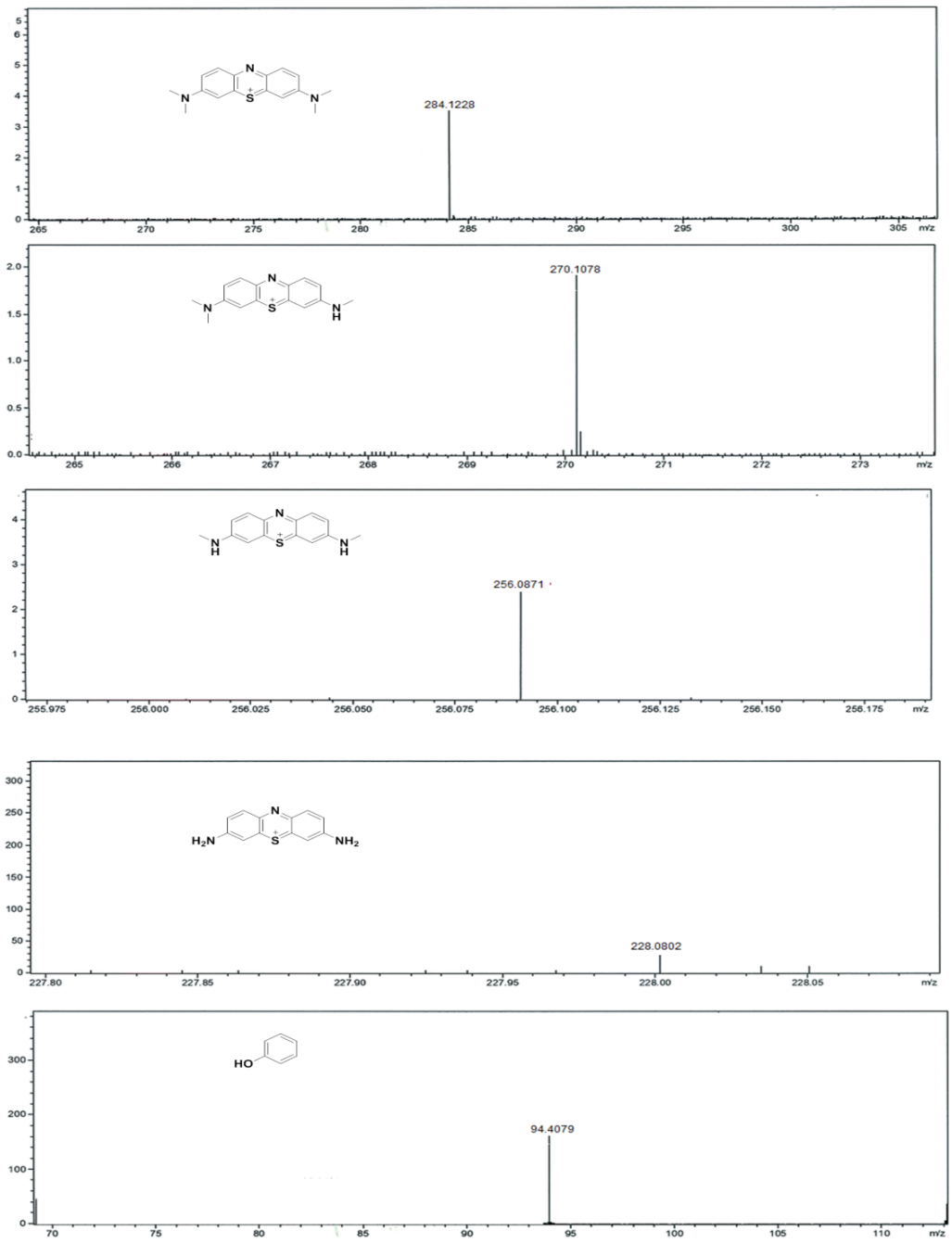


Fig. 6. LC/MS spectra for each intermediate from MB to phenol.

Conclusions

Highly efficient TiO_2/PA-11 photocatalyst was synthesized and applied to enhance the photocatalytic activity of towards photodegredation of methylene blue dye under visible light irradiations. It was observed that the photocatalytic activity for MB dye degradation rate under visible light irradiation was increased by using the photocatalyst TiO_2/PA-11 (200 ppm) under basic conditions for 2 h at room temperature.

Conflicts of interest

There are no conflicts to declare.

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