

# Efficient photodegradation of methyl violet dye using $\text{TiO}_2/\text{Pt}$ and $\text{TiO}_2/\text{Pd}$ photocatalysts

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**Abstract** Titanium oxide supported palladium ( $\text{TiO}_2/\text{Pd}$ ) and titanium oxide supported platinum ( $\text{TiO}_2/\text{Pt}$ ) nanoparticles were prepared from their precursors through the incipient wetness method. The  $\text{TiO}_2/\text{Pd}$  and  $\text{TiO}_2/\text{Pt}$  nanoparticles were characterized by scanning electron microscopy (SEM), and energy dispersive X-rays (EDX), while the photodegradation study of methyl violet was performed by UV/VIS spectrophotometry. The morphological study shows that the Pd and Pt were well deposited on the surface of  $\text{TiO}_2$ , which was confirmed by EDX. Both  $\text{TiO}_2/\text{Pd}$  and  $\text{TiO}_2/\text{Pt}$  nanoparticles were used as photocatalysts for the photodegradation of methyl violet in aqueous media under UV-light irradiation. The photodegradation study revealed that the  $\text{TiO}_2/\text{Pd}$  and  $\text{TiO}_2/\text{Pt}$  nanoparticles degraded about 95 and 78% of dye within 20 min, respectively. The effect of various parameters such as catalyst dosage, concentration of dye, and medium on the photocatalytic degradation was examined. The activity of recovered  $\text{TiO}_2/\text{Pd}$  and  $\text{TiO}_2/\text{Pt}$  nanoparticles was studied.

**Keywords**  $\text{TiO}_2$  · Photodegradation · Methyl violet · Photocatalyst

## Introduction

Photocatalyst is a semiconductor material (Kumar et al. 2008) activated by adsorbing photon and has the capability of accelerating a reaction without being consumed (Fox 1988). These semiconductor materials are used for heterogeneous photocatalysis, which is an advanced oxidation process of organic compound that leads its degradation to carbon dioxide, water and mineral ions (Garza-Tovar et al. 2006; Dai et al. 2013). This advanced oxidation process is based on generation of hydroxyl and superoxide anion radicals being responsible for the photocatalytic degradation of organic pollutants (Saeed et al. 2015a, b). It was also reported that the photocatalytic technique is the most promising technique for the wastewater treatment because it has advantages over the traditional techniques like quick oxidation, no formation of polycyclic products, and oxidation of pollutants up to the parts per billion (ppb) level (Chen et al. 2008).

Various photocatalysts were used for the degradation of dyes such as copper hexacyanoferrate(II) (Sharma and Sharma 2013), ZnO and Mn-doped ZnO (Ullah and Dutta 2008),  $\text{TiO}_2$  (Shrivastava 2012), etc. Among these photocatalysts,  $\text{TiO}_2$  has received greater attention due to its cheap availability, photoreactivity, non-toxicity, strong oxidizing power, chemical and biological inertness, and long-term photo-stability (Tolia et al. 2012; Mukhlis et al. 2013). Also it has the ability to degrade organic pollutants in water and atmosphere due to its chemical stability and suitable band gap energy (Zori 2011). However, the low separation efficiency of charges and relatively high recombination of photo-generated carriers limit the photocatalytic efficiency of  $\text{TiO}_2$  (Su et al. 2013).

In the present study, an approach is introduced to retard such charges recombining deficiencies by depositing noble metal on  $\text{TiO}_2$  surface. The loading of noble metals on

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TiO<sub>2</sub> surface increases its photocatalytic activity due to acceleration of hydroxyl radical formation and inhibits electron-hole recombination because it acts as an electron accepting species (Sakthivel et al. 2004). In our work, we prepared TiO<sub>2</sub>, TiO<sub>2</sub>/Pd and TiO<sub>2</sub>/Pt nanoparticles and used them as photocatalysts for the photodegradation of methyl violet dye. The methyl violet (triphenylmethane dye) was selected because it has a wide range of applications in different industries and in the staining of bacteriological and histopathological work. It imparts color to water even at very low concentration, which is harmful to aquatic and terrestrial life including human beings (Sarnaik and Kanekar 1999). The dye also causes severe skin and eye irritation, and gastrointestinal tract irritation if swallowed (Mittal et al. 2008). The morphological study and percentage of elements were determined by SEM and EDX, respectively, while photodegradation in the study was carried out by UV/VIS spectrophotometer. The efficacy of the recovered photocatalysts for degradation of dye in aqueous medium was also studied.

## Experimental work

### Materials

Titanium tetrachloride (TiCl<sub>4</sub>), platinum (IV) chloride (PtCl<sub>4</sub>) and palladium (II) chloride (PdCl<sub>2</sub>) were purchased from BDH. The sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) and NH<sub>3</sub> were supplied by Merck and Sigma-Aldrich, respectively. Methyl violet dye was purchased from Scharlau.

### Preparation of photocatalyst

TiO<sub>2</sub> was prepared by treating TiCl<sub>4</sub> with ice cold diluted H<sub>2</sub>SO<sub>4</sub> solution. The mixture was stirred vigorously for 30 min and then heated at 60 °C. The heated mixture was then cooled to room temperature for ammonolysis. A white precipitate of TiO<sub>2</sub> was obtained at pH 7, filtered and then washed with distilled water. The TiO<sub>2</sub> was dried and then calcined at 400 °C with heating rate 1 °C/min and the temperature was retained for 6 h.

TiO<sub>2</sub> supported Pd and Pt photocatalysts with metal contents ranging from 0.1 to 1.2 wt% were prepared by the incipient wetness method. A paste of TiO<sub>2</sub> was formed in the aqueous solution of PdCl<sub>2</sub> and PtCl<sub>4</sub> (containing calculated amount of Pt/Pd) and dried in an oven at 105 °C overnight. The sample was then subjected to calcination at 400 °C (1 °C/min) and maintained for 6 h at the same temperature. The calcined photocatalyst was pulverized and finally reduced in a mixture of H<sub>2</sub> and N<sub>2</sub> gases at a flow rate of 40 mL/min for 9 h at 240 °C.

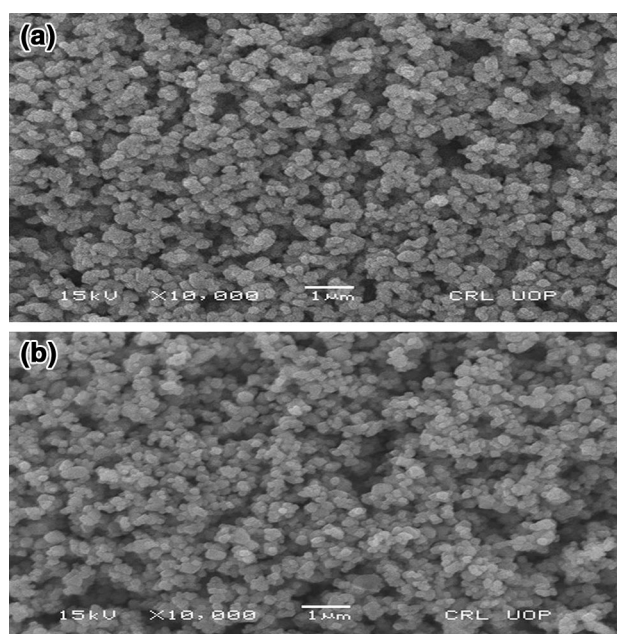


Fig. 1 SEM images of a TiO<sub>2</sub>/Pd, b TiO<sub>2</sub>/Pt

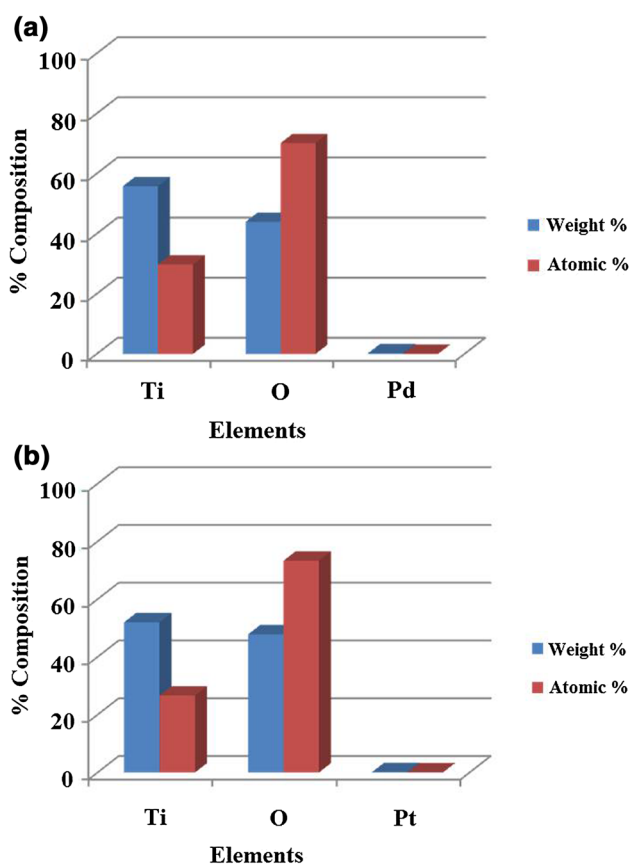
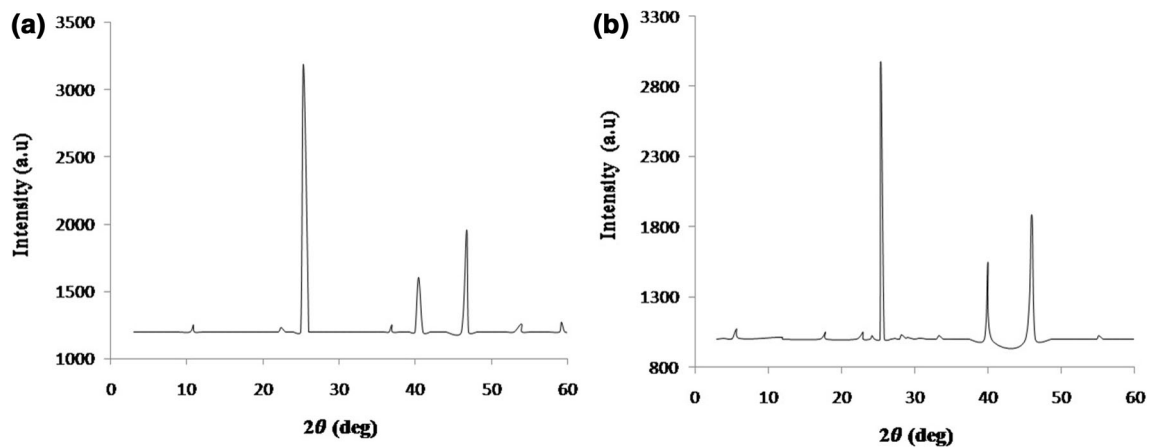
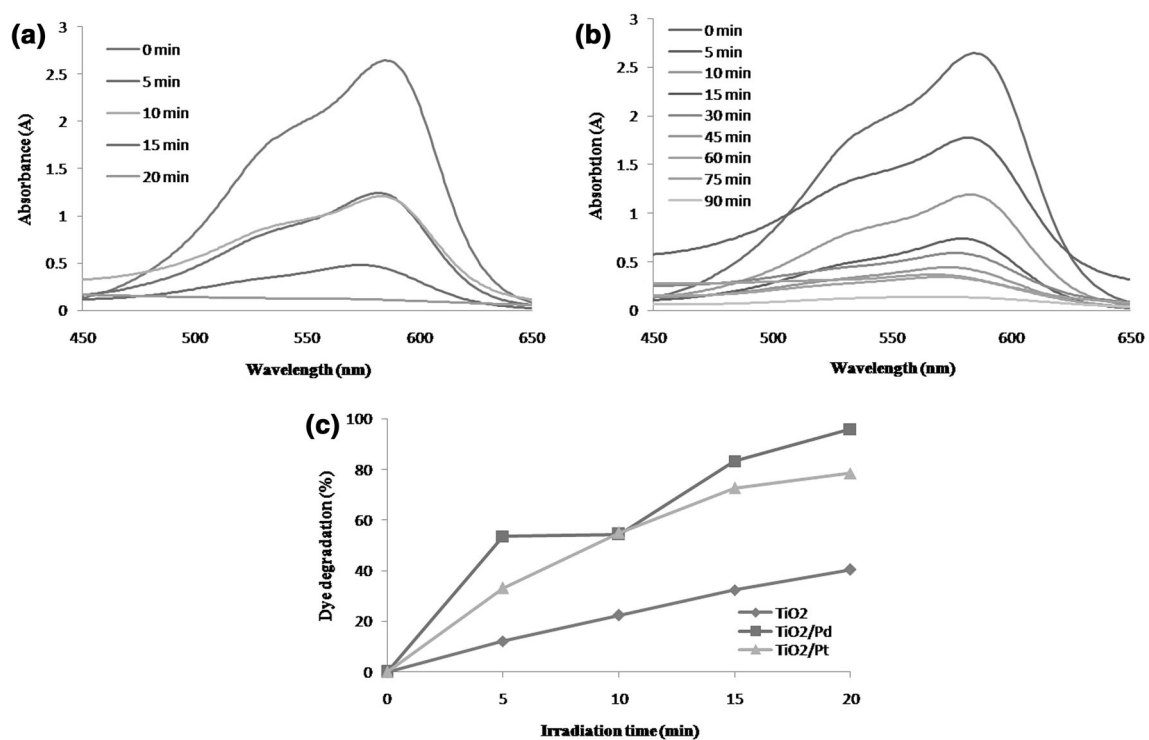


Fig. 2 EDX study of a TiO<sub>2</sub>/Pt and b TiO<sub>2</sub>/Pd



**Fig. 3** XRD patterns of **a** TiO<sub>2</sub>/Pt and **b** TiO<sub>2</sub>/Pd



**Fig. 4** UV–VIS absorbance spectra of MV degraded by **a** TiO<sub>2</sub>/Pd, **b** UV–VIS absorbance spectra of MV degraded by TiO<sub>2</sub>/Pt and **c** comparison of %degradation by both photocatalysts

### Photodegradation of methyl violet dye

10 mL of methyl violet (15 ppm) and 0.02 g of TiO<sub>2</sub>, TiO<sub>2</sub>/Pd and TiO<sub>2</sub>/Pt were taken separately in beakers and kept under UV-light (UV lamp having 254 nm, 15 W) with constant stirring. After specific irradiation time, the catalyst was separated by centrifugation (1200 rpm) and dye degradation was measured using UV–VIS spectrophotometry. The percent degradation of methyl violet in aqueous

medium was calculated by the following equation (Saeed et al. 2015a).

$$\text{Degradation rate (\%)} = \left( \frac{C_0 - C}{C_0} \right) \times 100$$

$$\text{Degradation rate (\%)} = \left( \frac{A_0 - A}{A_0} \right) \times 100$$

where  $C_0$  is the initial dye concentration,  $C$  is the dye concentration after UV irradiation,  $A_0$  shows initial

absorbance, and  $A$  shows the dye absorbance after UV irradiation.

## Characterization

The morphological study of gold-coated  $\text{TiO}_2/\text{Pd}$  and  $\text{TiO}_2/\text{Pt}$  was carried out by JEOL, JSM-5910 SEM. The EDX analyses of GNs/Sn-Pt were performed by EDX (model INCA 200/Oxford Instruments, UK). The photodegradation study of methyl violet was performed using a UV–VIS spectrophotometer (UV-1800, Shimadzu, Japan).

## Results and discussion

### SEM and EDX study

Figure 1 shows the SEM images of prepared  $\text{TiO}_2/\text{Pd}$  and  $\text{TiO}_2/\text{Pt}$  nanoparticles' photocatalysts. The SEM images showed that the Pd and Pt nanoparticles appeared on the surface of  $\text{TiO}_2$ . The size range of both  $\text{TiO}_2/\text{Pd}$  and  $\text{TiO}_2/\text{Pt}$  nanoparticles were below 500 nm as depicted from the micrographs. The presence of Pd and Pt on  $\text{TiO}_2$  surface was also confirmed by EDX (Fig. 2), which show that Pd and Pt nanoparticles are deposited onto titania. The result shows that about 0.24% Pd and 0.16 Pt % by weight were deposited on  $\text{TiO}_2$ .

### XRD analysis

Figure 3a and b shows the X-ray diffraction (XRD) pattern of the prepared  $\text{TiO}_2/\text{Pd}$  and  $\text{TiO}_2/\text{Pt}$ , respectively. The characteristic peaks at  $2\theta = 25^\circ$  and  $48^\circ$  are for the anatase phase of  $\text{TiO}_2$  nanoparticles, while no peaks were observed for brookite and rutile phases of titania. The peaks appearing at  $2\theta = 40.1^\circ$  and  $46.7^\circ$  indicate Pd, while the peaks appearing at  $2\theta = 40^\circ$  and  $46^\circ$  indicate Pt (Rashid et al. 2016).

### Photodegradation study of methyl violet

Figure 4 shows the efficiencies of both  $\text{TiO}_2/\text{Pd}$  and  $\text{TiO}_2/\text{Pt}$  photocatalysts in methyl violet degradation under UV-light irradiation. By increasing the radiation time the degradation of methyl violet dye can be increased as depicted by the UV/VIS spectra. The results also (Fig. 4) illustrated that the degradation efficiency of  $\text{TiO}_2/\text{Pd}$  nanoparticles was higher than  $\text{TiO}_2/\text{Pt}$  and pure  $\text{TiO}_2$  nanoparticles. Figure 4c shows the %degradation of methyl violet photodegraded by  $\text{TiO}_2$ ,  $\text{TiO}_2/\text{Pd}$  and  $\text{TiO}_2/\text{Pt}$ , which present that  $\text{TiO}_2/\text{Pd}$  and  $\text{TiO}_2/\text{Pt}$  nanoparticles degraded about 95 and 78% of dye within 20 min while pure  $\text{TiO}_2$  degraded about 40% dye within the same

irradiation time. The greater difference in such degradation is the deposition of noble metals on  $\text{TiO}_2$  surface, which inhibits recombining of separated charges. The general mechanism for photodegradation is that when photon is absorbed by  $\text{TiO}_2$ , excitation of electrons ( $e^-$ ) occurs from valence band to the conduction band and that results in positive holes ( $h^+$ ) in valence band. The  $e^-$  in the conduction band is accepted by the loaded noble Pd and Pt metals, which inhibit recombining deficiencies of created charges. The generated  $h^+$  reacts with  $\text{H}_2\text{O}$  molecules and generates  $\cdot\text{OH}$  radicals. While the  $e^-$  that is absorbed by loaded metals, reacts with adsorbed  $\text{O}_2$  molecules and form superoxide ions ( $\text{O}_2^-$ ). These generated hydroxyl and superoxide radicals are strong

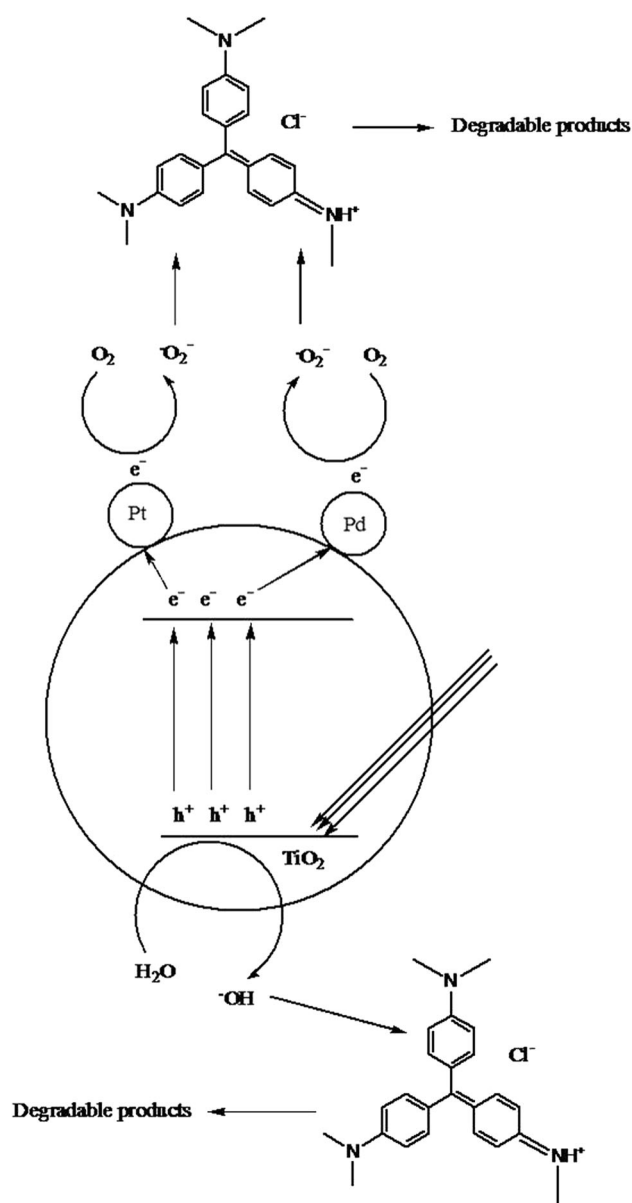
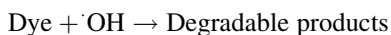
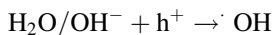
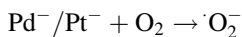
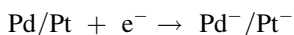
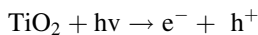


Fig. 5 Mechanism of photodegradation of methyl violet

oxidants, which attack the dye molecules and as a result degradation of dye molecules occur (Su et al. 2013; Sakthivel et al. 2004; Chnirheb et al. 2012). The major possible reactions are believed to be as follows, which is also illustrated in the Fig. 5.



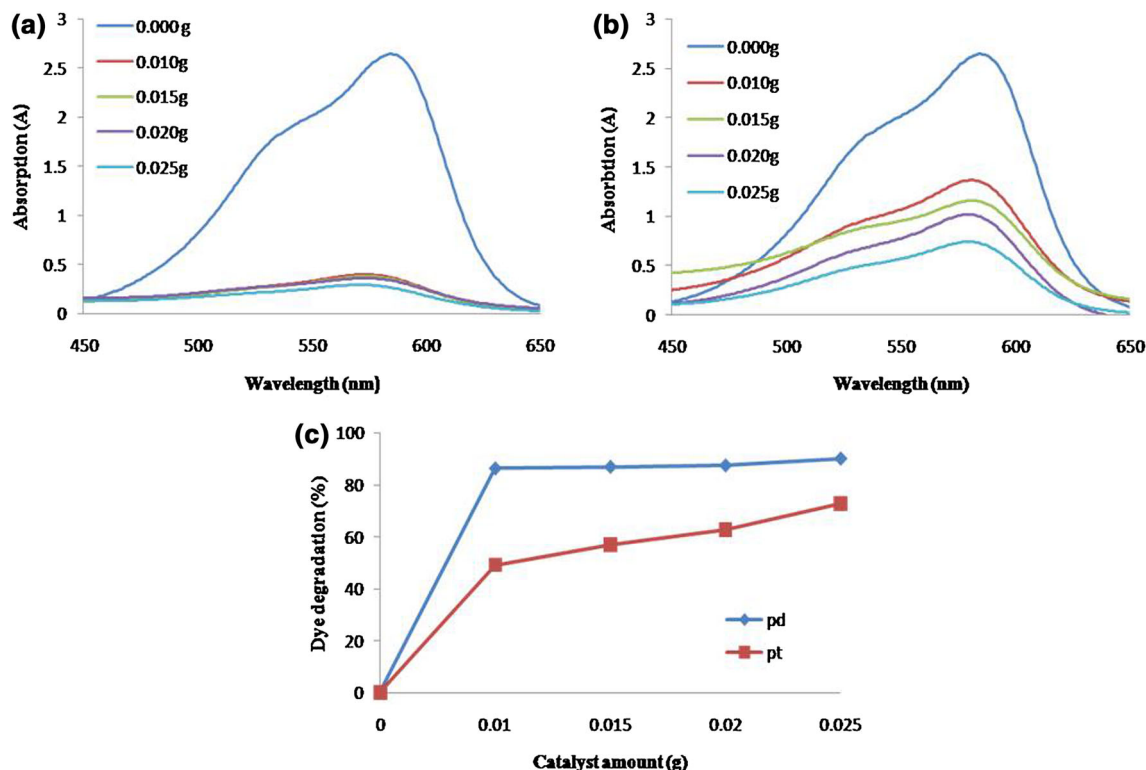
### Effect of photocatalysts dosage

The effect of photocatalysts dosage was also studied by loading different amount of photocatalyst (0.010, 0.015, 0.020 and 0.025 g) during photocatalytic reaction, where dye concentration (15 ppm) and irradiation time (15 min) remains constant. Figure 6 shows the UV/VIS spectra of methyl violet in aqueous media using different amount of  $\text{TiO}_2/\text{Pd}$  and  $\text{TiO}_2/\text{Pt}$  photocatalysts. The spectra illustrated (Fig. 6a, b) that the photodegradation of methyl violet

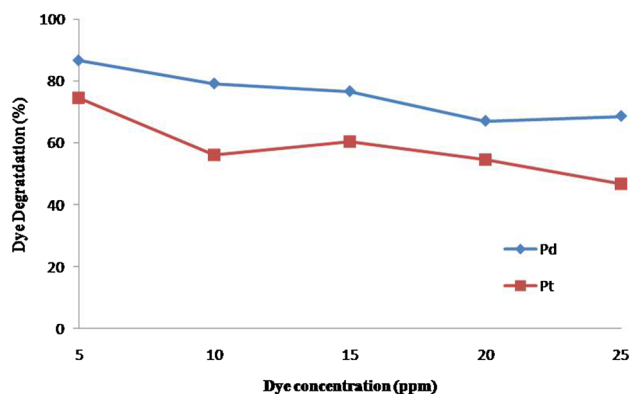
increased as increased the quantity of catalyst and then level off. The enhanced photodegradation of dye is due to increase in catalyst and as result active sites increased, which in turn to increase the number of hydroxyl and superoxide radicals. After that limit, degradation rate remains decreases or remains constant, which might be due to interception of light by suspension via increasing catalyst dosage from optimum limit. The possibility is the agglomeration of catalyst particles due to which surface for photon absorption become unavailable (Akpan and Hameed 2009). Figure 6c represents the comparison of %degradation of methyl violet dye using different amount of photocatalyst. The results show that 0.01 g of  $\text{TiO}_2/\text{Pd}$  nanoparticles degraded 86.3% dye, which increased gradually and about 90% of dye was degraded by using 0.025 g catalyst. Similarly, 0.01 g of  $\text{TiO}_2/\text{Pt}$  degraded 49% dye, which also increased gradually and highest degradation (72.6%) was obtained by adding 0.025 g of catalyst.

### Effect of dye concentration

The effect of dye concentration on photodegradation rate of methyl violet was also evaluated by studying photodegradation at various concentrations (5, 10, 15, 20 and 25 ppm) of dye. Figure 7 shows the %degradation of methyl violet using constant catalyst dosage and irradiated time



**Fig. 6** UV–VIS absorbance spectra of methyl violet degraded different catalyst dosage of **a**  $\text{TiO}_2/\text{Pd}$ , **b**  $\text{TiO}_2/\text{Pt}$  and **c** comparison of %degradation by different catalyst dosage



**Fig. 7** Comparison of %degradation by  $\text{TiO}_2/\text{Pd}$  and  $\text{TiO}_2/\text{Pt}$  at various dye concentrations

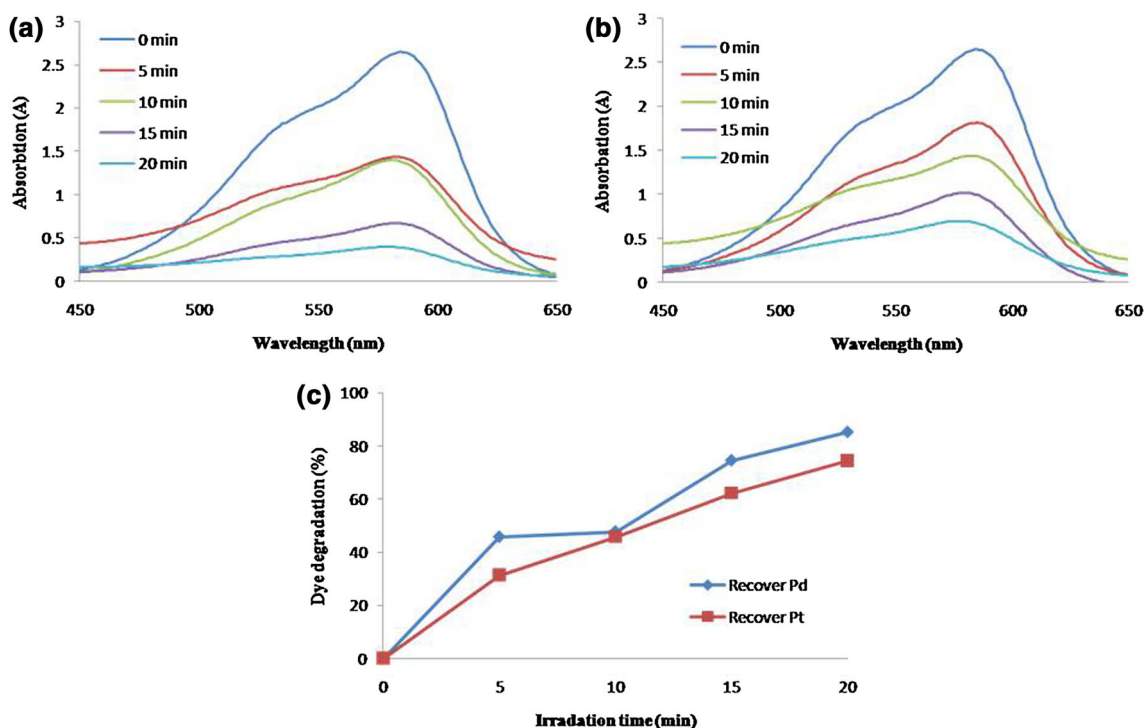
(15 min). The results revealed that the rate of photodegradation of dye decreased as increased the dye concentration. The possible reason is that as the initial concentration of dye increases, the molecules of dye get adsorb on catalyst surface, which absorb significant amount of UV-light rather than  $\text{TiO}_2$  particles. It also decreases the formation of hydroxyl radicals as dye molecules occupy active sites of photocatalyst (Reza et al. 2015). It is clear from the Fig. 7 that  $\text{TiO}_2/\text{Pd}$  and  $\text{TiO}_2/\text{Pt}$  decomposed about 86.6 and 74.5% dye at concentration of 5 ppm while at 25 ppm about 68.5 and 46.7% of dye degraded within 15 min.

### Effect of recovered catalyst on photodegradation of methyl violet

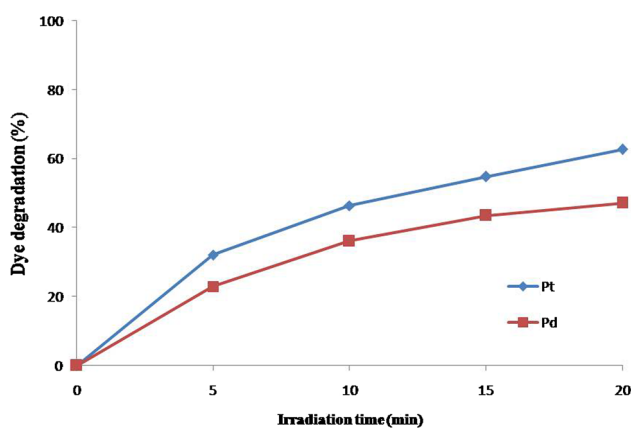
The efficiency of recovered catalysts was also studied by using it again for the degradation of methyl violet in aqueous medium under the same experimental conditions. The recovered catalysts show less catalytic activity as compared to original catalysts due to blocking of its active site by deposition of photosensitive hydroxides on the photocatalysts' surface (Ong et al. 2012). Figure 8a and b shows the UV–VIS spectra of methyl violet using recovered  $\text{TiO}_2/\text{Pd}$  and  $\text{TiO}_2/\text{Pt}$  photocatalysts. It was found that the photodegradation of dye increases by increasing the irradiation time. Figure 8c shows the %degradation of dye by recovered catalysts, which presented that recovered  $\text{TiO}_2/\text{Pd}$  and recovered  $\text{TiO}_2/\text{Pt}$  degraded methyl violet 85 and 74%, respectively, within 20 min.

### Effect of tap water

The effect of tap water on the photodegradation of methyl violet dye was also studied by preparing dye solution in tap water. Figure 9 shows the %degradation of methyl violet dye in tap water degraded by  $\text{TiO}_2/\text{Pd}$  and  $\text{TiO}_2/\text{Pt}$  photocatalysts. Results data show that  $\text{TiO}_2/\text{Pd}$  and  $\text{TiO}_2/\text{Pt}$  degraded less dye in tap water as



**Fig. 8** UV–VIS spectra of methyl violet degraded by recovered a  $\text{TiO}_2/\text{Pd}$ , b  $\text{TiO}_2/\text{Pt}$  and c comparison of %degradation by recovered  $\text{TiO}_2/\text{Pd}$  and  $\text{TiO}_2/\text{Pt}$



**Fig. 9** Comparison of %degradation of methyl violet dye in tap water by TiO<sub>2</sub>/Pd and TiO<sub>2</sub>/Pt

compared to dye degraded in deionized water under the same experimental conditions. The possible reasons for such deviations might be due to the presence of additional species in tap water such as organic, inorganic, and metallic ions, serve as competing species against catalyst active sites, hence reduce its activity (Banegas and Hartmann 2014). Results also illustrated that TiO<sub>2</sub>/Pd is less active than TiO<sub>2</sub>/Pt in tap water, which is against the normal condition as in deionized water. This might be due to the presence of chloride ions in tap water, which acting as competing species against catalyst active sites instead of dye molecules. The results indicated that TiO<sub>2</sub>/Pt degraded 62% dye while TiO<sub>2</sub>/Pd degraded about 47% dye under the same experimental conditions (time 20 min).

## Conclusion

It was concluded that both TiO<sub>2</sub>/Pd and TiO<sub>2</sub>/Pt nanoparticles are efficient catalysts for photodegradation of methyl violet dye in aqueous medium. It was also found that TiO<sub>2</sub>/Pd nanoparticles were more efficient as compared to TiO<sub>2</sub>/Pt nanoparticles. It was found that the rate of degradation is increased by increasing the irradiation time and catalyst dosage. While the rate of degradation is decreased by increasing the initial dye concentration. The methyl violet dye in aqueous medium was also significantly degraded by recovered catalysts.

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## References

- Akpan UG, Hameed BH (2009) Parameters affecting the photocatalytic degradation of dyes using TiO<sub>2</sub>-based photocatalysts: a review. *J Hazard Mater* 170:520–529
- Banegas E, Hartmann J (2014) Photocatalytic degradation of a series of commercial hair dyes using immobilized TiO<sub>2</sub>. BS thesis, Worcester Polytechnic Institute, Massachusetts United States
- Chen T, Zheng Y, Lin JM, Chen G (2008) Study on the photocatalytic degradation of methyl orange in water using Ag/ZnO as catalyst by liquid chromatography electrospray ionization ion-trap mass spectrometry. *J Am Soc Mass Spectrom* 19:997–1003
- Chnirheb A, Kanawati MHB, El Azzouzi M, Gebefugi I, Schmitt-Kopplin P (2012) Efficiency and degradation products elucidation of the photodegradation of mephenpyrdiethyl in water interface using TiO<sub>2</sub> P-25 and Hombikat UV100. *J Environ Sci* 24:1686–1693
- Dai K, Lu L, Dawson G (2013) Development of UV-LED/TiO<sub>2</sub> device and their application for photocatalytic degradation of methylene blue. *J Mater Eng Perform* 22:1035–1040
- Fox M (1988) Photocatalytic oxidation of organic substances. In: Kluwer (ed) *Photocatalysis and environment: trends and applications*. New York Academic Publishers, New York, pp 445–467
- Garza-Tovar LL, Torres-Martinez LM, Rodriguez DB, Giomez R, Angel GD (2006) Photocatalytic degradation of methylene blue on Bi<sub>2</sub> MNbO<sub>7</sub> (M = Al, Fe, In, Sm) sol–gel catalyst. *J Mol Catal A* 247:283–290
- Kumar PSS, Sivakumar R, Anandan S, Madhavan J, Maruthamuthu P, Ashokkumar M (2008) Photocatalytic degradation of Acid Red 88 using Au–TiO<sub>2</sub> nanoparticles in aqueous solutions. *Water Res* 42:4878–4884
- Mittal A, Gajbe V, Mittal J (2008) Removal and recovery of hazardous triphenylmethane dye, methyl violet through adsorption over granulated waste materials. *J Hazard Mater* 150:364–375
- Mukhlsh MZB, Najnin F, Rahman MM, Uddin MJ (2013) Photocatalytic degradation of different dyes using TiO<sub>2</sub> with high surface area: a kinetic study. *J Sci Res* 5:301–314
- Ong ST, Cheong WS, Hung YT (2012) Photodegradation of commercial dye, methylene blue using immobilized TiO<sub>2</sub>. 4th International conference on chemical, biological and environmental engineering, vol 43, p 109
- Rashid H, Sadiq M, Zia MA, Sadiq S, Ahmad MS, Aman R, Humayon M, Ali R (2016) Photooxidation of toluene: correlation of noble metal loading on titania and activation energy. *J Chem*. doi:10.1155/2016/4231467
- Reza KM, Kurny ASW, Gulshan F (2015) Parameters affecting the photocatalytic degradation of dyes using TiO<sub>2</sub>: a review. *Appl Water Sci*. doi:10.1007/s13201-015-0367-y
- Saeed K, Khan I, Park S-Y (2015a) TiO<sub>2</sub>/amidoxime-modified polyacrylonitrile nanofibers and its application for the photodegradation of methyl blue in aqueous medium. *Desalin Water Treat* 54:3146–3151
- Saeed K, Khan I, Shah T, Park S-Y (2015b) Synthesis, characterization and photocatalytic activity of silver nanoparticles/amidoxime-modified polyacrylonitrile nanofibers. *Fibers Polym* 16:1870–1875
- Sakthivel S, Shankar MV, Palanichamy M, Arabindo B, Bahnemann DW, Murugesan V (2004) Enhancement of photocatalytic activity by metal deposition: characterization and photonic efficiency of Pt, Au, and Pd deposited on TiO<sub>2</sub> catalyst. *Water Res* 38:3001–3008
- Sarnaik S, Kanekar P (1999) Biodegradation of methyl violet by *Pseudomonas mendocina* MCM B-402. *Appl Microbiol Biotechnol* 52:251–254

- Sharma O, Sharma MK (2013) Copper hexacyanoferrate(II) as photocatalyst: decolorisation of neutral red dye. *Int J Chem Tech Res* 5:2706–2716
- Shrivastava VS (2012) Photocatalytic degradation of methylene blue dye and chromium metal from wastewater using nanocrystalline TiO<sub>2</sub> semiconductor. *Arch Appl Sci Res* 4:1244–1254
- Su Y, Yang Y, Zhang H, Xie Y, Wu Z, Jiang Y, Fukata N, Bando Y, Wang ZL (2013) Enhanced photodegradation of methyl orange with TiO<sub>2</sub> nanoparticles using a triboelectric nanogenerator. *Nanotechnology* 24:295401
- Tolia JV, Chakraborty M, Murthy ZVP (2012) Photocatalytic degradation of malachite green dye using doped and un-doped ZnS nanoparticles. *Pol J Chem Technol* 14:16–21
- Ullah R, Dutta J (2008) Photocatalytic degradation of organic dyes with manganese-doped ZnO nanoparticles. *J Hazard Mater* 156:194–200
- Zori MH (2011) Synthesis of TiO<sub>2</sub> nanoparticles by microemulsion/heat treated method and photodegradation of methylene blue. *J Inorg Organomet Polym* 21:81–90