Indian Journal of Chemistry
Vol. 55A, April 2016, pp. 429-434

Synthesis and characterization of titania-magnetic activated carbon composite for photocatalytic degradation and mineralization of *p*-nitrophenol

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Received 12 May 2015; re-revised and accepted 21 March 2016

A novel, magnetically separable composite photocatalyst, titania coated with magnetic activated carbon, is prepared by depositing TiO_2 onto the surface of magnetic activated carbon which was prepared by directly adsorbing of magnetic Fe_2O_3 nanoparticles onto activated carbon. The samples are characterized by X-ray diffraction, scanning electron microscopy and vibration sample magnetometer. Specific surface area is determined by BET method and is found to be 381 m^2/g. The photocatalytic activity of the composite is determined by degradation of the model contaminant of water, i.e., *p*-nitrophenol. The degradation rate of *p*-nitrophenol by composite was higher than 90% after the composite was reused for five cycles. The synergy factor for the degradation of *p*-nitrophenol by titania coated with magnetic activated carbon was found to be 1.45. The composite can be easily separated by a magnet.

Keywords: Photocatalysts, Catalysts, Titania coated magnetic activated carbon, Magnetic activated carbon, Nitrophenol

With the development of industry and technology, environmental pollution is one of the most serious problems faced by mankind today. Heterogenous photocatalysis as an effective technique has received great attention for the purification of polluted air and wastewater[1-3]. Due to the use of dioxygen, light and completely mineralized organic and inorganic substrates, especially biorecalcitrant, advanced oxidation process is considered to be environmentally friendly. Photocatalysis is based upon the use of UV irradiated semiconductors, such as titanium dioxide (TiO_2), to eliminate various organic pollutants. TiO_2 has been extensively studied for environmental purification applications, due to its good photocatalytic activity, high stability, non-toxicity and inexpensiveness[4-5].

Finely dispersed TiO_2 has large reactive surface area, but it is difficult and cost intensive to separate and recover these nanoparticles from liquid phase[6]. In order to enhance the immobility or separability of the photocatalysts, some researchers have prepared titania-coated hollow glass beads[7], titania based thin film[8] and titania-coated magnetic particles (e.g. Fe_3O_4, Fe_2O_3)[9]. However, the activity of titania photocatalysts in the photocatalytic system reduces considerably because the effective surface area of photocatalyst decreases significantly after immobilization[10]. To enhance the effective surface area and maintain the photocatalytic activity, the titania nanoparticles are immobilized on supports with high surface area, such as zeolite, alumina, silica, activated carbon (AC)[11-14]. It is well known that activated carbon is one of the low-cost and widely available porous materials with relatively large surface area. Commercial ACs have been widely used as adsorbents and catalytic supports in liquid media to remove contaminants, and to recover valuable products[14]. Matos *et al.*[15] investigated the photocatalytic degradation of aqueous organic pollutants by a suspended mixture of titania and AC. They found that photocatalytic activity increased, on account of synergistic effect and a common contact interface between TiO_2 and AC. However, the separation and recovery problems still existed in practical applications because the AC supported catalyst was micron grade size. It has been shown that magnetic particles could be easily separated from suspension system[10]. Thus, a composite photocatalyst combining large surface area and magnetic separability would be an attractive and practical option.

In the present work, we have synthesized magnetically separable composite photocatalyst, viz., titania coated magnetic activated carbon, by depositing MAC *in situ* on TiO_2 prepared by sol-gel method. The synergism between MAC and TiO_2 has also been studied. The prepared samples are characterized by XRD, SEM, BET and VSM. The photocatalytic activity and recyclability of the prepared composite is evaluated by degradation of synthetic wastewater containing the model pollutant, *p*-nitrophenol (PNP) under UV irradiation. PNP was selected as targeted pollutants because of its environmental importance. It is considered as a priority toxic pollutant by the United States

Environmental Protection Agency (US EPA). PNP is one of the refractory substances present in industrial wastewater and shows high stability and solubility in water. The maximum allowed concentration of PNP in water is 20 ppb (ref. 16). Even at very low concentrations, it causes chronic poisoning. PNP is used in the production of pesticides like parathion and nitrofen and synthetic dyes[17-18]. It is also used as insecticides and herbicides. Since it has significant water solubility (1.6 g/100 mL), it is often present in wastewater discharges from such facilities. It may also be found in ground water wells and surface waters where it has to be removed in order to achieve drinking water quality[19]. A long period of incubation is required for the microbial degradation of PNP[20]. Considering all these hazardous aspects of PNP, the choice of said pollutant for the present study is justified.

Experimental

Analytical reagent (AR) grade chemicals were used throughout the present study and were employed without further purification. AC, Hydraffin C-30 granular activated carbon, which is used for the wastewater purification was procured from Lurgi Aktivkohle GmbH Germany. This carbon is characterized by a very high surface area of 800 m^2/g, moisture content (<5 wt %) and particle size (0.5-2.5 mm), as per the information provided by the manufacturer. Titanium tetraisopropoxide (TTIP) was purchased from Spectrochem, India. PNP was purchased from Sisco Research Laboratory, Pvt. Ltd, India. $FeCl_3.6H_2O$, $FeSO_4.7H_2O$, Conc. HCl, Conc. HNO_3, NH_3 were procured from S D Fine Chem Limited, India. Isopropanol was purchased from Merck, India.

Synthesis of TMAC was carried out in three stages as follows:

(1) The magnetic nanoparticles (MNs) were synthesized by chemical co-precipitation method. $FeSO_4.7H_2O$ (0.1 *M*) and $FeCl_3.6H_2O$ (0.1 *M*) were taken in 1:2 molar ratio and was precipitated by 2.5% NH_3. Part of the precipitate was taken out and washed several times with water and dried in an oven.

(2) For the synthesis of MAC, AC was activated according to the method described in the literature[21]. The dried powder (10g) was refluxed with 125 mL 20% HNO_3 and 125 mL 20% H_2SO_4 at 110 °C for 90 min. The refluxed mixture was filtered and washed with distilled water several times and finally dried at 60 °C overnight. AC (4 g) was sonicated in distilled water for 30 mins separately and then added to the precipitated solution and stirred for 1 h. The solution was kept for ageing and the product (MAC) was isolated with a permanent magnet, washed with distilled water several times and then dried at 110 °C in an oven for 1 h.

(3) For the synthesis of TMAC, TiO_2 was prepared by sol-gel method using TTIP precursor. TTIP diluted with isopropanol was added dropwise with continuous stirring into the distilled water whose acidity was adjusted with conc. HNO_3. The solution was stirred for 1 h and was kept under reflux condition for 24 h at 70 °C. Finally, pure TiO_2 was obtained by drying the solution at 100 °C. To obtain TMAC, dip coating procedure was used. MAC (1g) was dispersed in TiO_2 sol under ultrasonic for 1.5 h. Subsequently, the obtained wet catalyst was dried at 80 °C.

MNs, MAC, TMAC were characterized by, X-ray diffraction, scanning electron microscopy, BET surface area analysis and vibrating sample magnetometery (VSM). XRD patterns were recorded on a X-ray diffractometer (XRD) (Phillips PW1729), equipped with Cu anode and graphite monchromator. The diffractograms were recorded by using Cu-Kα radiation over a 2 θ range of 20° – 80°. Scanning electron microscopy (Jeol JSM-6360) was used to characterize the morphology of the MNs, MAC and TMAC composite. Magnetization properties were investigated by vibrating sample magnetometery (VSM) which quantified the magnetic behaviour. The BET surface areas of the synthesized catalysts were measured by using the BET surface area analyzer (Smart Sorb 90) using nitrogen as the adsorbate. The sample was out gassed at 200 °C for 2 h before the analysis.

Photocatalytic experiments were carried out with 100 mL of 1.0×10^{-4} *M* PNP aqueous solution using 40 mg TMAC as photocatalyst under exposure to UV irradiation in a multilamp photoreactor constituting four 8W low pressure mercury vapor lamps at 30±1 °C. Air was bubbled through the reaction solution from the bottom using an aerator with constant speed. The entire reactor assembly was mounted on a magnetic stirrer for mixing the aqueous solution during the reaction to ensure that the solution was well-mixed and the catalysts did not settle down inside the container (Supplementary data, Fig. S1). During photocatalytic experiments, the slurry containing aqueous PNP solution and TMAC was magnetically stirred for 10 mins in dark to attain adsorption- desorption equilibrium between the PNP molecules and the catalyst. It was then irradiated and an aliquot (1 mL) was withdrawn at specific time intervals and filtered to separate the catalyst through millipore disc (0.2 µm, 13 mm dia.). Changes in absorption spectra were recorded at λ_{max} on a UV-visible spectrophotometer (Schimadzu UV-1650).

Recyclability and reuse of photocatalyst is one of the key steps to develop heterogeneous photocatalysis technology for practical applications. Recycling and reusability of TMAC was evaluated to examine the photoactivity in each cycle. After being used in one cycle, for 90 minutes irradiation, the composite was separated by a magnet, dried and then reused for another cycle. The above procedure was repeated for five cycles.

Results and discussion

XRD patterns of prepared samples are presented in Fig. 1. TiO_2 deposited on MAC has an anatase structure in the TMAC sample, where the peaks (25.4 °, 38.0 °,48.0 °,54.7 °) are the characteristics peaks of anatase structural TiO_2.

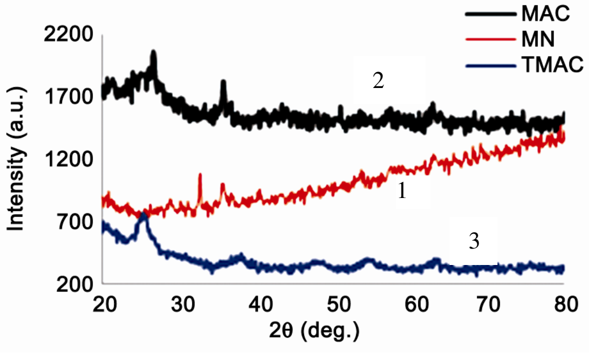

Fig. 1 – XRD patterns of (1) MN, (2) MAC, and, (3) TMAC.

SEM photographs show that MNs are spherical in shape (Fig. 2a), while Fig. 2(b&c) reveals the deposition of MN on AC and MAC on TiO_2 respectively. Specific surface area was calculated by using single point method and was found to be 800, 562, 381 and 105 m^2/g for AC, MAC, TMAC and TiO_2 respectively. The surface area of TMAC increased 3.6 times as compared to TiO_2 causes increased rate of photocatalytic degradation of PNP.

Magnetization properties were investigated by vibrating sample magnetometery, which is used to study magnetic behavior of a material. The saturation magnetization (M) of MNs was found to be 25 emu/g. In contrast, the saturation magnetization of TMAC was found to be 0.5 emu/g, (Fig. 3a & 3b). This is attributed mainly to the relative low content of magnetic particles in TMAC sample due to the non-magnetic coating layer. However, the coating of AC and TiO_2 does not change the magnetic properties of the magnetic material. Thus, magnetic property of TMAC composite is retained which is useful for the separation of catalyst.

The photocatalytic activity of TiO_2 and TMAC was studied by the degradation of PNP under UV irradiation. The blank study indicated that mere photolysis can be ignored as it is only 4.7% after being illuminated for 90 min. As can be seen in

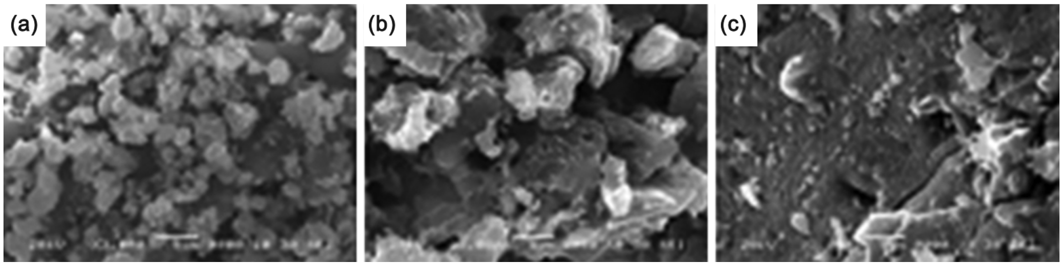

Fig. 2 –SEM images of (a) MN, (b) MAC, and, (c) TMAC.

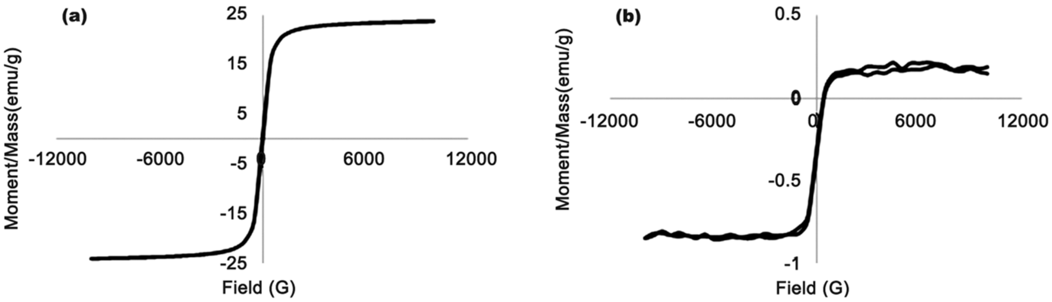

Fig. 3 – VSM of (a) MN and (b) TMAC.

Fig. 4, depositing MAC on TiO_2 increases the photocatalytic activity of TiO_2. The enhanced photocatalytic activity can be explained by two reasons: one is the small size effect of TiO_2. MAC inhibits the aggregation of TiO_2 nano particles, hence TiO_2 particles formed in the composite are more effective than pure TiO_2. The other reason is the synergistic effect of MAC adsorption and TiO_2 photocatalysis. These results indicate that TMAC exhibits an enhanced photocatalytic performance. Rate of degradation of PNP was found to be in the order: TMAC > TiO_2. The percentage degradation of PNP by TiO_2 and TMAC was found to be 84% and 94% respectively, after being illuminated for 90 mins. Rates of degradation of PNP by AC and MAC are comparable. AC and MAC showed only adsorption and no photocatalysis, which is evident from the similar degradation of PNP in presence as well as in absence of UV (Table 1). Therefore, it is just a simple transformation of pollutant from one phase to another, causing secondary pollution. The changes in the absorption spectra of photocatalytic degradation of PNP by TMAC is shown in Fig. 5. The decrease of absorption peak intensity at 318 nm confirms the degradation and mineralization of PNP.

The degradation and mineralization of the targeted pollutant (PNP) was confirmed by chemical oxygen demand (COD) analysis. The PNP solution was oxidized by excess amount of $K_2Cr_2O_7$ in presence of conc. H_2SO_4 and Ag_2SO_4 at 150 °C for 2 using COD digester (Spectralab COD digestor 2015M). The excess amount of $K_2Cr_2O_7$ was evaluated by carrying out titration with ferrous ammonium sulfate using COD titrator (Spectralab COD titrator CT-15). The dichromate consumed gives the amount of O_2 required for the oxidation of the organic matter. The results were calculated in ppm using the following formula:

$$\text{COD (mg/L)} = (\text{A-B})\times\text{normality of } Fe(NH_4)_2(SO_4)_2 \times 8\times 1000/\text{amt of sample (mL)}$$

where A = amt of $Fe(NH_4)_2(SO_4)_2$ (0.1 *N*) added for blank and B = amt of $Fe(NH_4)_2(SO_4)_2$ (0.1 *N*) added for the sample.

The reduction in COD was found to be 70% for the degradation of PNP by TMAC composite in contrast with 64% by TiO_2 as photocatalyst. COD data reveal that there is substantial degradation and mineralisation for PNP when TMAC composite was used as a photocatalyst.

The mechanism of semiconductor photocatalysis is well estabilished[22]. The addition of MAC to TiO_2 increases the efficiency of degradation. The synergy factor has been estimated quantitatively using Eq. (1) as reported for AC–TiO_2[23]. The synergistic effect of TMAC is shown by the synergy factor of 1.45, is depicted in Fig. 6. The TMAC system showed significant improvement in photoreactivity as compared to bare TiO_2 due to the synergistic effect of TiO_2 and MAC. The proposed mechanism of the synergistic enhancement in TMAC composite is depicted in Fig. 7. For comparison, the mechanism of bare TiO_2 is shown in Fig. S2 (Supplementary data). In the absence of MAC support, pollutants must adsorb on TiO_2 surface for the photocatalytic reaction to occur. When this is not achieved, pollutants and other photocatalytic degradation intermediates will

Table 1 – Photodegradation of PNP in presence and absence of UV

Irradiation time (min)	C/C_0	
	AC+UV	Only AC
0	1.000	1.000
10	0.090	0.078
30	0.022	0.030
60	0.010	0.020
90	0.007	0.010

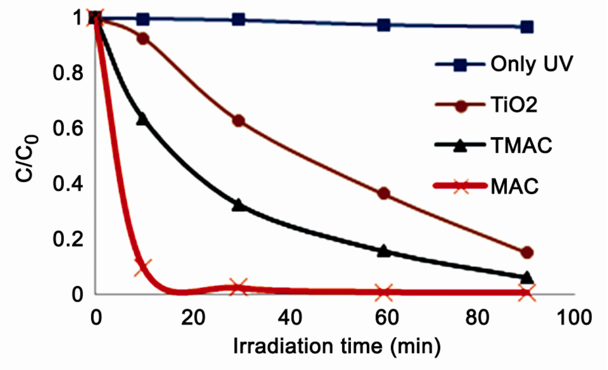

Fig. 4 – Photocatalytic degradation of PNP by TiO_2 ,TMAC, only UV, and, MAC.

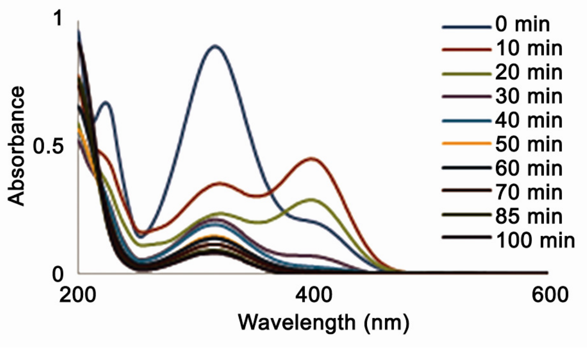

Fig. 5 – Absorption spectra of photocatalytic degradation of PNP by TMAC.

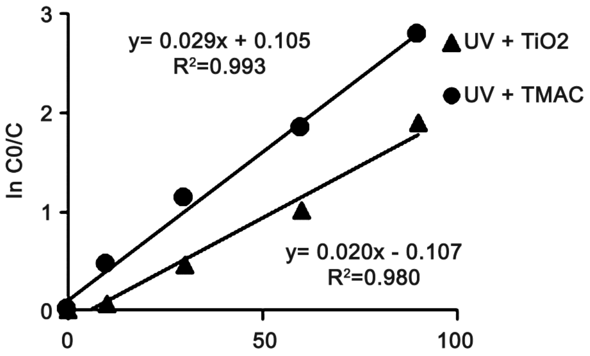

Fig. 6 – Kinetic plot for the photocatalytic degradation of PNP by TiO_2 and TMAC.

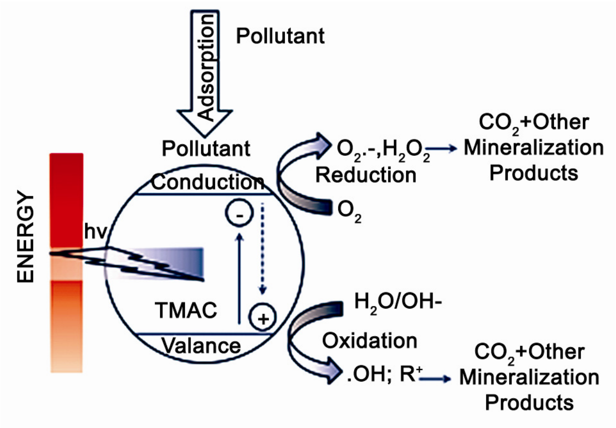

Fig. 7 – Proposed mechanism of synergistic enhancement in TMAC composite.

pass back into the solution and can only react further when they are adsorbed on TiO_2 again[24]. However, when MAC is used as a support, increased adsorption of pollutants onto TMAC provides a high concentration of pollutants on the surface of the composite, thereby enhancing the photocatalytic activity of the composite. During photocatalytic degradation on TMAC, the intermediates formed also get adsorbed on MAC which allows further degradation to occur. The concentration of pollutants onto TMAC is increased due to increased adsorption of pollutant molecules as there is 3.6 times increase in the BET surface of TMAC as compared to TiO_2.

$$R = \frac{k_{\text{app}}\,(\text{TMAC})}{k_{\text{app}}\,(\text{TiO}_2)} \qquad \ldots (1)$$

Recyclability and reuse of photocatalyst is an important factor in the development of heterogenous photocatalysis technology for practical applications. The role of magnetic material is the effective separation of the composite TMAC from the treated solution by applying a magnet, regeneration and reuse of the composite. Herein, the separation problem of photocatalyst was solved without depressing the activity of TiO_2 by depositing it onto MAC. The TMAC composite was separated by external magnetic field after photcatalytic degradation, washed several times by water and ethanol and dried. The dried composite samples were used for the degradation of PNP at similar experimental conditions. Even in the fifth cycle, the photocatalytic activity was almost as high as the first cycle. The degradation percent was higher than 90%. Thus, the composite, TMAC, maintained its high photocatalytic activity on repetitive use and may be suitable for practical detoxification of wastewater. The study also suggests that separation of photocatalyst by the magnetic field was effective.

In the present study, we have illustrated a simple route for successfully synthesizing the composite TMAC by depositing TiO_2 on MAC. The composite thus prepared was able to degrade synthetic wastewater containing PNP. The new composite can be reused without any mass loss. Even after 5 cycles, the degradation rate of PNP was higher than 90%. The synergy factor of TMAC was shown to be 1.45. The TMAC system showed significant improvement in photoreactivity as compared to bare TiO_2 due to the synergistic effect of TiO_2 and MAC. From a practical point of view, TMAC composite may be suitable for large scale wastewater treatment in slurry reactor due to its high photocatalytic activity and easy separability.

Supplementary data

Supplementary data associated with this article, viz., Figs S1 and S2, are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_55A(04)429-434_SupplData.pdf

Acknowledgement

We are thankful to Board of Control and University Development (Fin/2012-13/824), and UPE II Savitribai Phule Pune University, Pune, Maharashtra, India for research funding.

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