

Photocatalytic membrane of a novel high surface area TiO₂ synthesized from titanium triisopropanolamine precursor

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Photocatalytic membrane was successfully prepared using an efficiently high surface area TiO₂ catalyst, dispersed into polyacrylonitrile matrix. The catalyst was directly synthesized using titanium triisopropanolamine as a precursor. The membranes were characterized using FT-IR, TGA, SEM and their photocatalytic performance tested, viz. stability, permeate flux and photocatalytic degradation of 4-NP. We find that polyacrylonitrile is an effective matrix, showing high stability and low permeate flux. The amount of TiO₂ loaded in the membrane was varied between 1, 3 and 5 wt% to explore the activity and stability of membranes in the photocatalytic reaction of 4-NP. As expected, the higher the loading of TiO₂ loaded, the higher the resulting catalytic activity. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: mixed matrix membrane; photocatalysis; 4-nitrophenol; titanium triisopropanolamine

INTRODUCTION

The use of mixed matrix membranes (MMM), i.e. membranes containing microencapsulated TiO₂, is of increasing interest because of their high selectivity combined with outstanding separation performance, processing capabilities and low cost, when polymers are used as the matrix. Many researchers^{1–4} have explored ways to develop and facilitate the separation process, using very thin microencapsulated membranes to allow for high fluxes. Such a membrane must have a high volume fraction of homogeneously distributed encapsulated particles in a defect- and void-free polymer matrix.⁵ Polymeric membranes are not appropriate for use in membrane reactor applications where high temperatures are needed for reaction. Thus, application of MMM for catalysis of low temperature reactions has become a main topic for many researchers, examples being hydrogenation

of propyne,⁶ photomineralization of *n*-alkanoic acids,⁷ wet air oxidation of dyeing wastewater, and photocatalytic oxidations.^{8–11}

The heterogeneous photocatalysis process harnesses radiant energy from natural or artificial light sources to degrade organic pollutants into their mineral components.¹² TiO₂ is a well-established catalyst for photocatalytic degradation due to its combination of high activity, chemical stability and non-toxic properties. Photocatalytic degradation generally occurs via production of OH• radicals. The organic pollutant is attacked by hydroxyl radicals and generates organic radicals or intermediates.^{13–16} The main drawback to practical implementation of the photocatalysis method arises from the need for an expensive liquid–solid separation process due to the formation of milky dispersions upon mixing the catalyst powder with water.¹⁷

Currently, this drawback is solved by the use of a TiO₂ membrane, consisting of fine TiO₂ particles dispersed in a porous matrix. Such titania membranes have attracted a great deal of attention in recent years due to their unique characteristics, including high water flux, semiconducting properties, efficient photocatalysis and chemical resistance relative to other membrane materials, such as silica and γ -alumina.¹⁸

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To obtain a high photocatalytic activity, the surface area of catalyst is very important. Thus, in our work, thermally stable TiO_2 with high surface area is synthesized from moisture-stable titanium triisopropanolamine. The performance of this material as a component of an MMM was evaluated in a photocatalytic membrane reactor, using 4-nitrophenol as a model substrate, with regard to stability tests and TiO_2 loading.

EXPERIMENTAL

Materials

Titanium dioxide (surface area $12 \text{ m}^2/\text{g}$) was purchased from Sigma-Aldrich Chemical Co. Inc. (USA) and used as received. Ethylene glycol (EG) was purchased from Malinckrodt Baker Inc. (USA) and purified by fractional distillation at 200°C under nitrogen atmosphere before use. Triethylenetetramine (TETA) was purchased from Facai Polytech. Co. Ltd (Bangkok, Thailand) and distilled under vacuum (0.1 mmHg) at 130°C prior to use. Triisopropanolamine (TIS) was purchased from Sigma-Aldrich Chemical Co. Inc. (USA). 4-Nitrophenol was purchased from Sigma-Aldrich Chemical Co. Inc. (USA).

Titanium tri-isopropanolamine precursor preparation and characterization

A mixture of TiO_2 (2 g, 0.025 mol), triisopropanolamine (9.55 g, 0.05 mol) and triethylenetetramine (3.65 g, 0.0074 mol) was stirred vigorously in excess ethylene glycol (25 cm^3) and heated to 200°C for 24 h. The resulting solution was centrifuged to separate the unreacted TiO_2 . The excess EG and TETA were removed by vacuum distillation at 150°C to obtain a crude precipitate. The product was characterized using FTIR, FAB^+ -MS and TGA. Fourier transform infrared spectra (FT-IR) were recorded on a VECOR3.0 Bruker spectrometer with a spectral resolution of $4/\text{cm}$. Thermal gravimetric analysis (TGA) was carried out using a Perkin Elmer thermal analysis system with a heating rate of $10^\circ\text{C}/\text{min}$ over a 30 – 800°C temperature range. The mass spectrum was obtained on a Fison Instrument (VG Autospec-ultima 707E) using the positive fast atomic bombardment mode (FAB^+ -MS) with glycerol as the matrix, cesium gun as initiator and cesium iodide (CsI) as a standard for peak calibration.

FT-IR: 3400 ($\sqrt{\text{OH}}$), 2927 – 2855 ($\sqrt{\text{C-H}}$), 1460 ($\delta\text{C-H}$ of CH_2 group), 1379 ($\delta\text{C-H}$ of CH_3 group), 1085 ($\sqrt{\text{C-O-Ti}}$), 1020 ($\delta\text{C-N}$) and $554/\text{cm}$ ($\sqrt{\text{Ti-O}}$); TGA: decomposition transition at 365°C with 16.60% ceramic yield (theoretical ceramic yield of 18.65%); FAB^+ -MS: $\text{Ti}([\text{OCHCH}_3\text{CH}_2]_2\text{N}[\text{CH}_2\text{CHCH}_3\text{OH}])_22\text{H}^+$ at m/e 428.

High surface area TiO_2 preparation and characterization

After removal of any excess solvent from titanium triisopropanolamine precursor, the precursor was transferred to a crucible and calcined at 600°C for 2 h at heating rate of

$0.25^\circ\text{C}/\text{min}$. TiO_2 was characterized by various techniques. The XRD pattern was obtained using a D/MAX-2200H Rigaku diffractometer with $\text{CuK}\alpha$ radiation on specimens prepared by packing sample powder into a glass holder. The diffracted intensity was measured by step scanning in the 2θ range of 5° to 90° . Thermal stability was characterized on a Perkin Elmer thermal analysis system with a heating rate of $10^\circ\text{C}/\text{min}$ over 30 – 800°C temperature range. Samples pyrolyzed at 600°C were analyzed using SEM by attachment onto aluminum stubs after coating with gold via vapor deposition. Micrographs of the pyrolyzed sample surfaces were obtained at $\times 7500$ magnification. Specific surface area and nitrogen adsorption–desorption were determined using an Autosorp-1 gas sorption system (Quantachrome Corporation) via the Brunauer–Emmett–Teller (BET) method. A gaseous mixture of nitrogen and helium was allowed to flow through the analyzer at a constant rate of $30 \text{ cm}^3/\text{min}$. Nitrogen was used to calibrate the analyzer and also used as the adsorbate at liquid nitrogen temperature. The samples were thoroughly outgassed for 2 h at 150°C , prior to exposure to the adsorbent gas.

Membrane preparation and characterization

A 10 wt% mixture of polyacrylonitrile powder in dimethyl formamide (DMF) was vigorously stirred at 50°C until homogeneous. A specified amount of TiO_2 was added to the stirred polymer solution. Partial vacuum was applied for a brief duration to ensure the removal of air bubbles. The mixture was then coated on a clean glass plate using a casting knife. The resulting membrane was allowed to set for 2 min before being dried in a vacuum oven at 40°C overnight following by 60°C for 2 h and 80°C for 2 h. The prepared membrane with thickness of $15 \mu\text{m}$ was cut into a circular shape with a diameter of 6 cm.

The membrane made was characterized using SEM and TGA. The morphology of membranes was analyzed by attachment onto aluminum stubs and coated with gold via vapor deposition. The membranes were frozen in liquid nitrogen and fractured to examine the cross-sectional areas. The samples were characterized on a Jeol 5200-2AE (MP 15152001) scanning electron microscope. The samples were also analyzed using Perkin Elmer thermal analysis system with a heating rate of $10^\circ\text{C}/\text{min}$ over 30 – 500°C temperature range to determine the organic residue in the prepared membranes

Stability tests of prepared membranes

The experiment was carried out to check the stability of prepared polymeric membrane (PAN) by placing the prepared membranes in a Petri dish containing either distilled water or 40 ppm 4-NP solution with and without irradiation for 6 h. The solutions were then withdrawn and analyzed for total organic carbon (TOC) to verify the organic components released from the membrane.

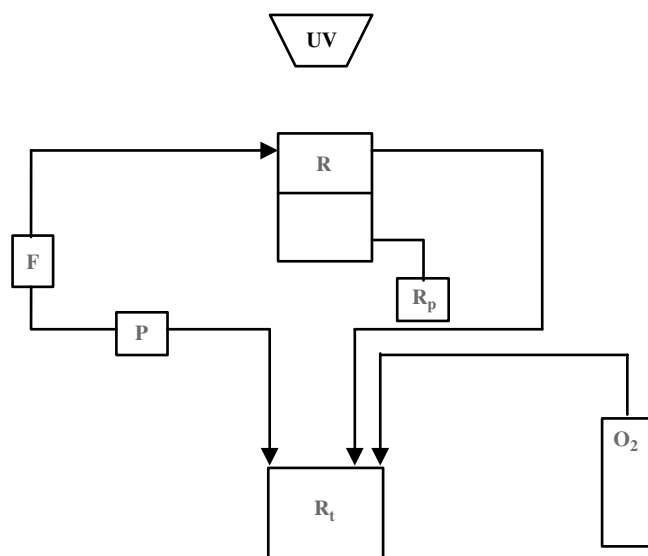


Figure 1. Schematic diagram of photocatalytic membrane reactor (F, flowmeter; R, reactor; R_p, permeate reservoir; R_t, recirculating tank; and P, peristaltic pump).

Photocatalytic decomposition of 4-nitrophenol

The photocatalytic reactions were carried out in a 1000 ml continuous batch glass reactor, Fig. 1, with gas inlet and outlet at an O₂ flow rate of 20 ml/min. A cooling water jacket was used to maintain the temperature at 30 °C. The suspensions and membrane were illuminated using a 100 W Hg Philip UV lamp. The concentration of 4-NP used was 40 ppm and the solution was continuously stirred. The obtained permeate was removed at 1 h intervals and analyzed to determine the concentration of 4-NP using a Shimadzu UV-240 spectrophotometer. For different pH value, H₂SO₄ was used to adjust the pH value measured using an Ecoscan pH meter.

RESULTS AND DISCUSSION

TiO₂ catalyst preparation

High surface area TiO₂ catalyst was characterized using XRD, TGA, BET and SEM to confirm the presence of the active anatase phase of TiO₂. The TGA thermogram (not given) illustrates absence of organic species, meaning the formation of pure TiO₂, while the XRD pattern shown in Fig. 2, exhibits diffraction peaks at $2\theta = 25.28, 37.94, 47.98, 54.64, 62.58, 69.76, 75.26$ and 82.72 . The average grain size of calcined TiO₂ calculated from Scherrer equation, is 12.42 nm. The SEM micrograph (not shown) presents similar particle morphology of the prepared anatase phase of TiO₂ to those in the literature.^{19–21} The surface area measurement shows a high surface area of 163 m²/g; also, the nitrogen adsorption–desorption isotherm of this material exhibits type IV character (Fig. 3), indicative of a mesoporous structure.

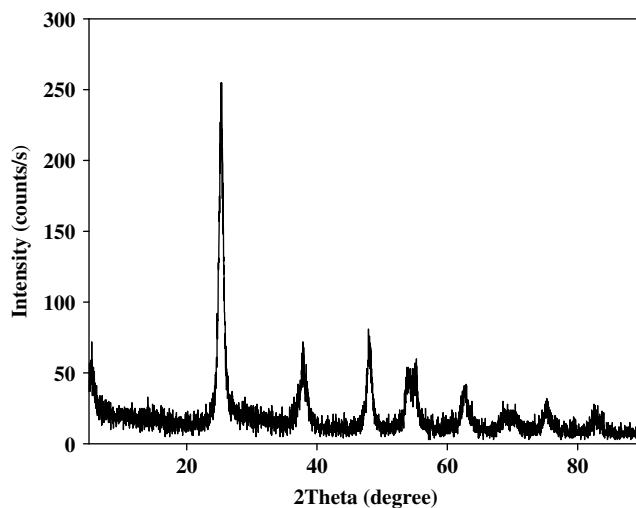


Figure 2. XRD pattern of the anatase phase of the prepared TiO₂ catalyst after calcinations of the precursor at 600 °C for 2 h.

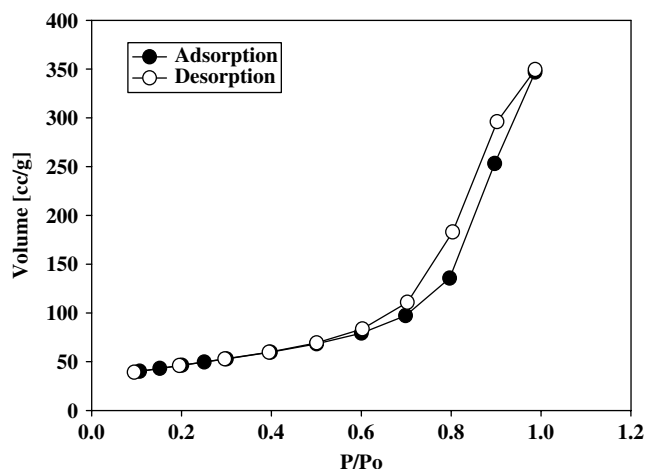


Figure 3. Nitrogen adsorption–desorption isotherm for the prepared mesoporous titania calcined at 600 °C.

Membranes preparation

The prepared mixed matrix membranes were characterized with respect to their purity using TGA thermogram and their morphology using scanning electron microscopy (SEM). The TGA thermogram (not given) gives only one transition at around 300 °C, referring to the degradation of PAN membrane,^{22,23} respectively. An SEM micrograph of the surface of the prepared membrane is shown in Fig. 4(a). When the TiO₂ particles are immobilized within the polymeric matrix, the micrographs reveal no evidence for the presence of voids between the polymer and TiO₂, implying that the membranes are dense. TiO₂ particles are well distributed across the surface. As varying the percentage of TiO₂ between 1, 3 and 5 wt%, morphological analysis by SEM, as shown in

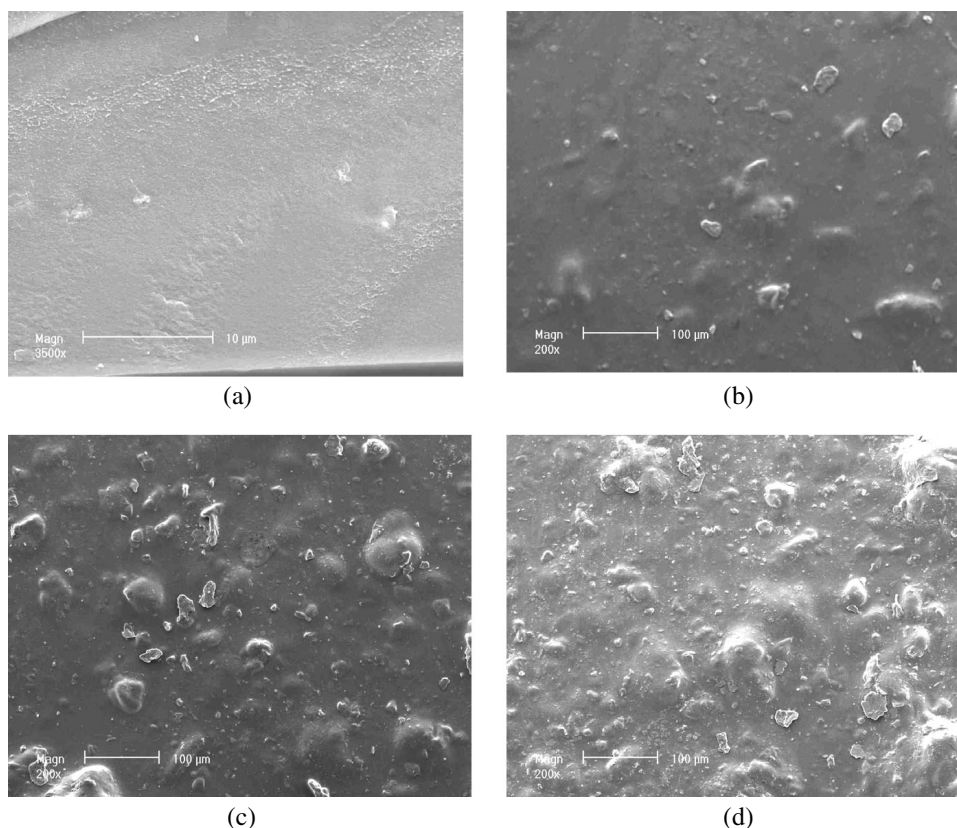


Figure 4. SEM micrographs of mixed matrix membranes using (a) polyacrylonitrile (PAN), (b) PAN + 1 wt% TiO₂, (c) PAN + 3 wt% TiO₂ and (d) PAN + 5 wt% TiO₂.

Fig. 4(b–d), indicates, TiO₂ particles are dispersed throughout the PAN matrix at all loadings.

Stability tests of prepared membranes

The stability of the prepared PAN membranes is summarized in Table 1, presenting the TOC results of the tested membrane. It was found that the PAN membrane is undoubtedly stable even under irradiation conditions.

The photocatalytic degradation of 4-nitrophenol

The photocatalytic activity of the PAN membrane was assessed using the photoreactor, employing 1 wt% immobilized photocatalyst TiO₂, oxygen flow rate of 20 ml/min, 4-NP flow rate of 30 ml/min and 4-NP concentration of 40 ppm at pH 3.^{9,10,24} The permeate flux data (not shown) indicate that the prepared PAN membrane has constant low

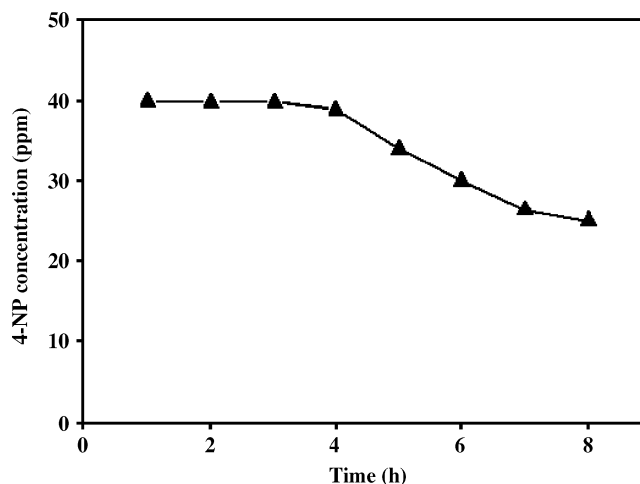


Figure 5. The degradation of 4-NP with the reaction time of the PAN membranes performed at pH 3.

Table 1. The stability tests of the prepared membranes

Membrane type and condition	TOC value at initial (ppm)	TOC value after 6 h (ppm)
PAN + H ₂ O + UV	0	0
PAN + 4-NP + UV	22.35	22.34
PAN + 4-NP	22.35	22.36

permeate flux level, 5.31 l/h m². The efficiency of the PAN membrane for photocatalytic degradation of 4-NP is illustrated in Fig. 5, which indicates that, at 1 wt% Ti loading in PAN membrane, the degradation of 4-NP occurs faster after 4 h irradiation.

Effect of various amounts of TiO₂ in PAN membrane on the photocatalytic degradation of 4-nitrophenol

4-NP auto-photolysis was first carried out without the mixed matrix membrane and showed no degradation. The experiment was thus performed to study the permeate flux of PAN membranes at the three loading levels, 1, 3 and 5 wt% of TiO₂ (Fig. 6). We found that the flux is constant for all three samples, and increases with the amount of TiO₂ from 5.3, to 8.1 to 12.7 l/h m², respectively. In Fig. 7, the efficiency of degradation of 4-NP at the three loading levels of TiO₂ is reported. The decrease of 4-NP at 3 and 5% loadings appears to be faster than at 1%. The reason may be that the TiO₂ loading is too low to see any differences in the degree of degradation of 4-NP. However, when compared with literature results,¹¹ performed at much higher loadings of TiO₂, it appears that these membranes show a higher level of catalytic activity.

Commercial TiO₂ (Degussa P25) was also studied for comparison with our TiO₂ at loading level of 3 wt%. The result, see Fig. 8, indicates no permeation of 4-NP through a membrane prepared using commercial TiO₂ and the efficiency of degradation of 4-NP measured from the retentate of two membranes shows that the degradation of 4-NP in the membrane prepared using our TiO₂ is distinguishably lower.

Effect of pH on degradation of 4-nitrophenol

From the literature, the rate of 4-NP decomposition at lower pH is faster and shows the highest activity at pH 3.^{9,10,24} Therefore, we compare the experiment of 4-NP solution at pH = 3 (adjust pH value of 4-NP solution by H₂SO₄) with pH = 7 (without the pH adjustment of 4-NP solution). It was found that the results indeed are the same after irradiation, see Fig. 9. The 4-NP concentration at pH = 3 declines sharply when applied the UV irradiation and reaches to the complete degradation after 8 h reaction time. Only 25% degradation occurs in the solution having pH = 7. Figure 10

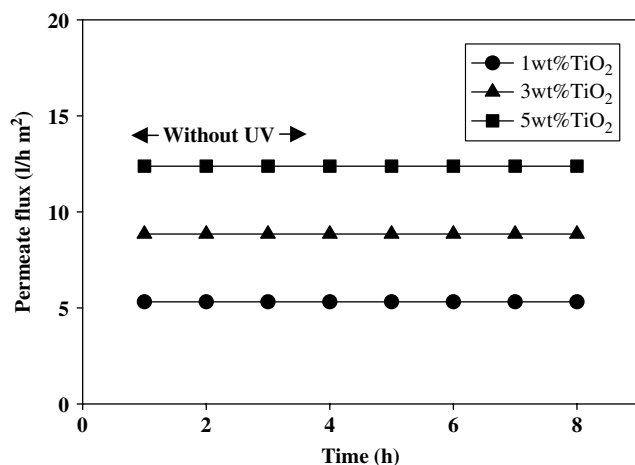


Figure 6. The permeate flux vs reaction time of polyacrylonitrile membranes at various percentages of TiO₂ and pH 3.

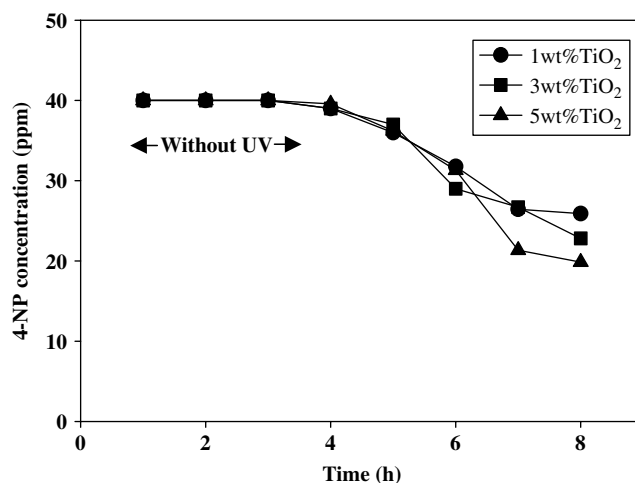


Figure 7. The degradation of 4-NP with the reaction time of polyacrylonitrile membranes at various percentages of TiO₂ and pH 3.

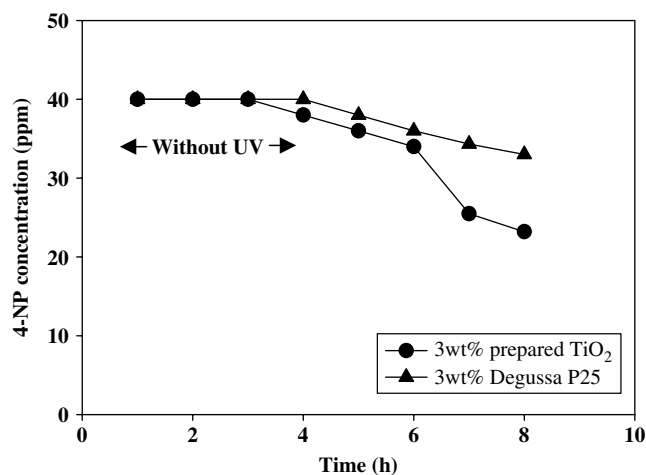


Figure 8. Effect of TiO₂ type mixed in the polyacrylonitrile membrane on the degradation of 4-NP.

shows the UV spectra of 4-NP concentration at pH = 3 in which the 4-NP is completely degraded. The surface of TiO₂ is positively charged in acidic media, therefore, the higher H⁺ concentration leads to the higher OH radicals for the photodegradation of 4-NP.²⁵

CONCLUSIONS

The titanium triisopropanolamine precursor can be prepared by a very simple method (the oxide one pot synthesis) from low cost starting materials, and yields a TiO₂ catalyst with high surface area obtained after calcinations of the precursor at 600 °C for 2 h. Polymeric membranes loaded with the as-prepared TiO₂ catalyst show an impressively

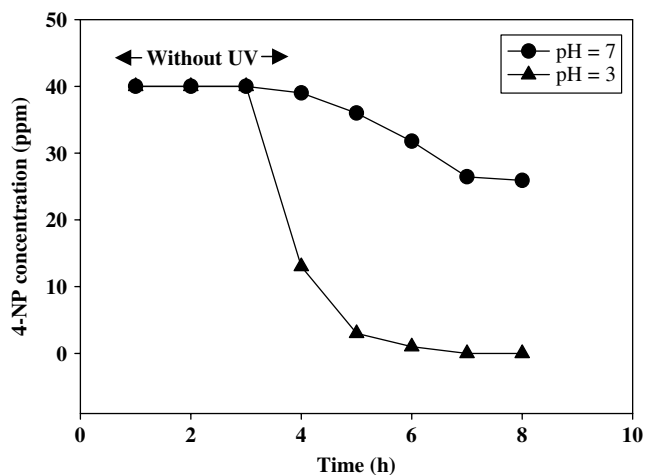


Figure 9. Effect of pH on the degradation of 4-NP using 3 wt% TiO_2 loaded in the polyacrylonitrile membrane.

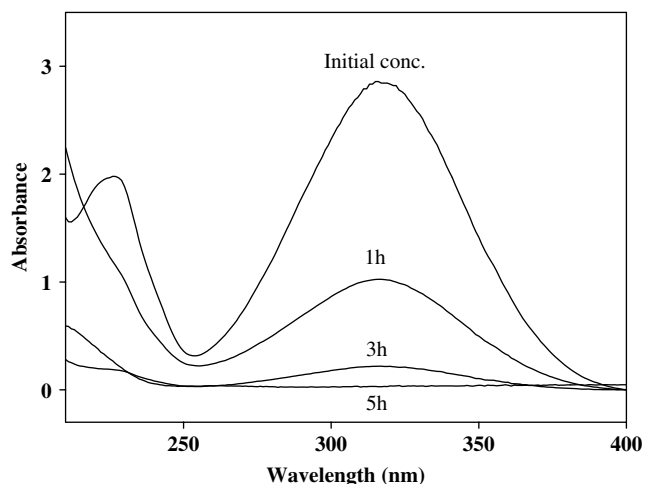


Figure 10. The UV spectra of 4-NP solution analyzed at different reaction time and pH = 3 using 1 wt% TiO_2 loaded in the polyacrylonitrile membrane.

high efficiency for the photocatalytic degradation of 4-NP. Examination of the properties of the PAN membrane indicates that it has considerably high stability low permeate flux. The photocatalytic degradation of 4-NP increases with increasing percentage of TiO_2 loaded in the PAN membrane. Higher

efficiency of photocatalytic degradation of 4-NP is illustrated at lower pH value.

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