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Photodegradation of polyaromatic hydrocarbons over thin film of TiO_2 nanoparticles; a study of intermediate photoproducts

Bonamali Pal *, Maheshwar Sharon

Department of Chemistry, Indian Institute of Technology, Powai, Mumbai-400 076, India

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Abstract

The photocatalytic degradation of saturated aqueous solution of naphthalene and anthracene was studied over thin films of porous TiO_2 particles on glass substrate, prepared by sol–gel process. Surface morphology and structural features were studied by SEM, TEM and Laser Raman Spectroscopy. These films have been found to be very efficient and the total photomineralisation of these organics to carbon dioxide and water occurs in air-equilibrated solution within 1 h. Concentration changes linearly with the illumination time, and high rate constants are obtained for the degradation of these organics. The pH of the solution changes with the irradiation time due to the formation of intermediate photoproducts, e.g., 5,8-dihydroxynaphthaquinone, and 9,10-anthraquinone, etc. Photodegradation mechanism and the detection of reaction intermediates have been discussed in details. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Photodegradation; Polyaromatic hydrocarbon; TiO_2 thin films

1. Introduction

Heterogeneous photocatalysis [1–9] is attracting a great deal of interest as a method of water purification, because of its low cost, and because the technique does not use any external chemical for purification. In the photocatalytic process, organic compounds are oxidised mainly to carbon dioxide when they come in contact with titanium dioxide powder illuminated with near UV light or sunlight. The most widely studied [10–14] chemicals are: phenol, chlorophenol, and other halogenated aromatic and aliphatic organics, which are very common toxic pollutants in industrial effluents. Usually, the titanium dioxide is used as a powder suspension. But filtration and separation of colloidal TiO_2 particles from the decontaminated water becomes a troublesome process. Alternatively, it has been reported [3,9,10] that titanium dioxide could be attached to glass surfaces allowing the TiO_2 to be illuminated as a stationary phase with water passing over the catalyst. Recently, dip coating from sol solution has attracted much attention as a simple method of preparing nanocrystalline semiconductor thin films. These films are found to possess very interesting optoelectronic properties and higher catalytic activity. O'Regan et al. [15], as well as Spanhel and

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* Corresponding author. Catalysis Research Center, Hokkaido University, Sapporo-060-0811, Japan. Fax: +81-11-709-4748.

E-mail address: pal@cat.hokudai.ac.jp (B. Pal).

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Anderson [16], developed the preparation of thin films of TiO_2 and ZnO nanoparticles by spin or dip coating from a concentrated colloidal solution on indium-tin oxide coated glass. Final heating of these films results in nanoporous film, in which the colloidal particles are tightly attached to the glass surface. The systematic investigations of photocatalytic transformation of anthracene-1-sulfonate [17], naphthalene [18–20], anthracene [20,21] and other polyaromatic hydrocarbons [21,22] in the aqueous TiO_2 suspension and their plausible degradation kinetics have been recently reported. Fox et al. [23] have reported the oxidative degradation of substituted naphthalenes over TiO_2 in O_2 saturated acetonitrile solutions. Though degradation of such polyaromatic hydrocarbons has been studied with TiO_2 slurries, there are few reports [4,10] available regarding the photooxidation of these hydrocarbon and their systematic study over thin film of TiO_2 particles. The present work describes the photodegradation pathway of aqueous solution of naphthalene and anthracene over nanocrystalline porous TiO_2 thin film on glass substrate.

2. Experimental section

2.1. Thin film preparation

Titanium dioxide films were prepared with the sol–gel process over glass substrate. This process is also advantageous because it is capable of producing photocatalysts with high surface area and high reactivity. The TiO_2 sol solution was prepared by mixing 5 ml titanium tetraisopropoxide in 50 ml isopropanol under vigorous stirring and kept at 0°C. Afterwards, the mixture was allowed to undergo partial hydrolysis at this temperature by the dropwise addition of isopropanol and hydrochloric acid with constant stirring. This colloidal preparation was stable for a long time. TiO_2 gel film was obtained by dipping the substrate in sol solution and pulling it up manually at constant speed. Then, it was dried in air for some time and was subjected to heat treatment under the atmosphere of air for 10 min at 400°C. This process was repeated for 5–6 times in order to get a film of desired thickness. The final sintering has been done at 400°C and 800°C for 4 h.

2.2. Materials and methods

Titanium—isopropoxide (Aldrich chemical), isopropanol, naphthalene and anthracene (Spectrochem) of AnalaR grade were used without any further purification. All photocatalytic experiments were carried out in a rectangular reaction chamber with one side having a quartz window through which light illumination was provided with a 125 W Hg lamp. The solution was stirred magnetically and air was purged continuously. Thin film of TiO_2 sintered at 400°C was placed inside the reaction chamber vertically near the quartz window with a support. The concentrations of the different solutions were analysed by UV–Vis spectrophotometer and spectrofluorimeter. Naphthalene and anthracene were analysed using excitation wavelengths 275 and 254 nm, respectively. Reaction intermediate photoproducts were detected using FTIR and GC-MS spectroscopy. Carbon

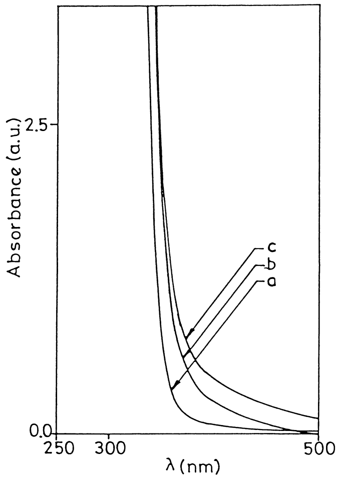


Fig. 1. Absorption spectra of TiO_2 sol taken at various time: (a) 5, (b) 30 and (c) 80 min after the addition of HCl.

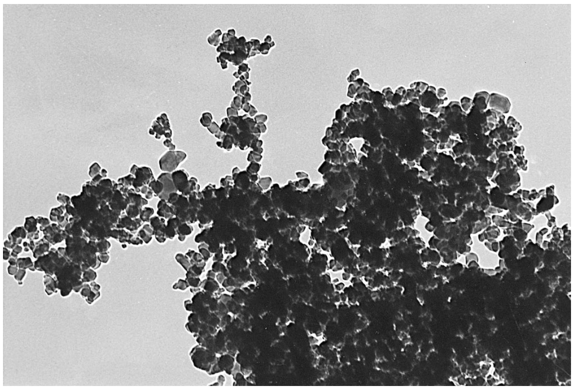


Fig. 2. TEM micrograph (1 cm = 150 nm) of TiO_2 powders taken from the film after sintering at 400°C.

dioxide has been measured with NUCON Gas Chromatograph using Porapak-Q column at room temperature and thermal conductivity detector at highest sensitivity using argon (30 ml/min) as a carrier gas and the injection volume was 10 μl.

3. Results and discussion

3.1. Characterisation of TiO_2 thin films

The UV–Vis absorption spectra of the TiO_2 sol for different time after the addition of HCl to the isopropanolic solution of titanium tetraisopropoxide are shown in Fig. 1. Immediately after mixing the HCl solution, the onset of absorption appears at about 360 nm. Afterwards, with the progress of hydrolysis, the absorption onset shifted to 380–400 nm. This shift in absorption onset is due to the growth of TiO_2 particles in colloidal solution and forming cluster with the progress of aging time. The particle size of the TiO_2 powder (taken from the film after sintering at 400°C) has been determined by using TEM. Fig. 2 shows the size distribution of TiO_2 particles on the film surface. Particle size, varying between 30 and 60 nm, and nonspherical crystals are seen in the TEM micrograph.

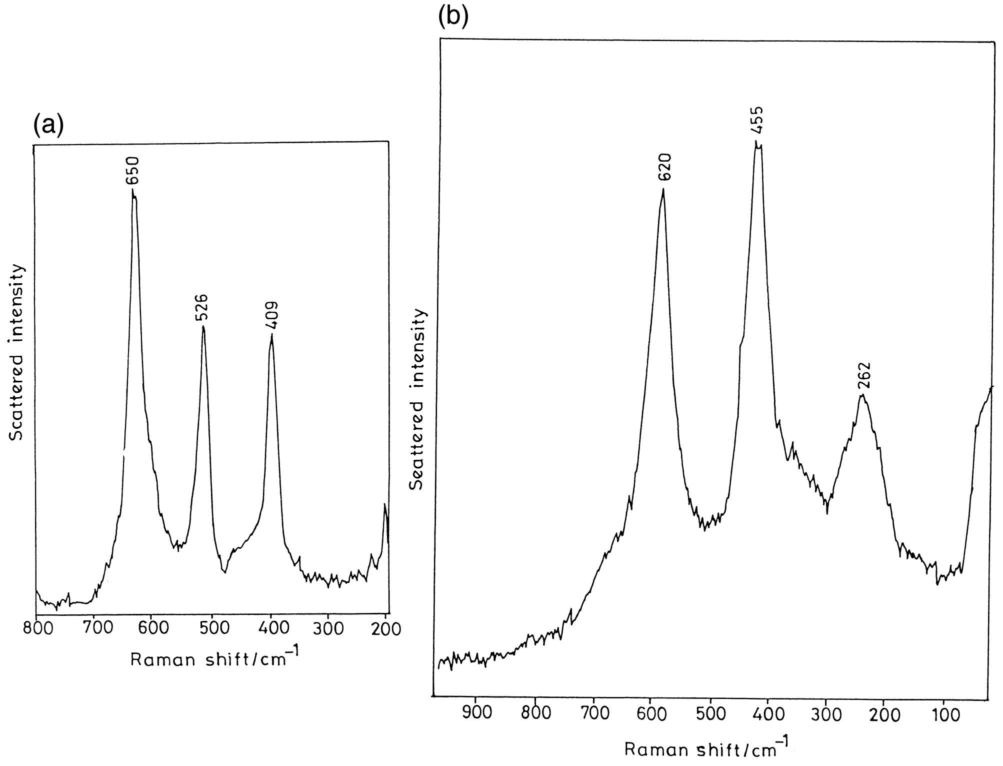


Fig. 3. Laser Raman spectra of the TiO_2 films sintered at (a) 400°C (anatase) and (b) 800°C (rutile).

This size falls typically in the range of nanosize particles. The film heated at 400°C shows anatase structure, and the film heated at 800°C shows rutile structure. Photodegradation experiments were carried out with the films heated at 400°C because higher catalytic activity of the anatase phase is expected at these temperatures. For further confirmation, the information about the vibrational characteristics of the films was derived by Laser Raman Spectroscopy. Fig. 3 shows the Laser Raman Spectra of the films heated at 400°C and 800°C. The peak positions and relative intensities correspond exactly to those of anatase and rutile structures at two different sintering temperatures, respectively. In anatase structure, the three main intense peaks appeared at 401, 516 and 640 cm^{-1}, and in rutile structure, the two main peaks appeared at 445 and 610 cm^{-1}, along with a broad peak at around 252 cm^{-1}. Melendress et al. [24] also found the similar type of low wave number peak at 240 cm^{-1} in nanophase titania particles and attributed to a second order scattering process or latent anharmonicity in the rutile phase. Fig. 4 shows the surface morphology of the films heated at 400°C. The SEM figures are shown at two different magnifications. At 400°C,

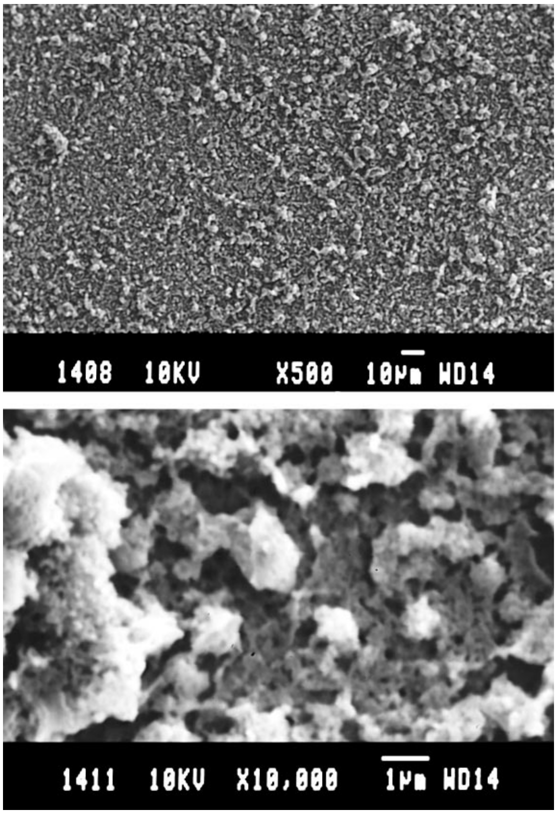


Fig. 4. SEM micrograph of the TiO_2 thin film at two different magnifications, sintered at 400°C.

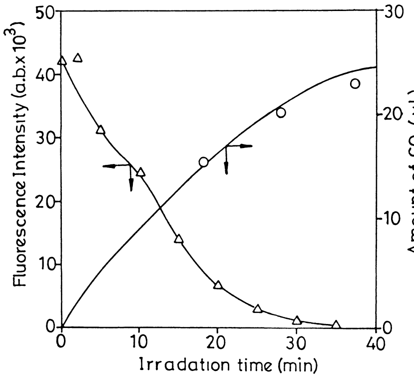


Fig. 5. Decrease in fluorescence intensity and the formation of CO_2 during the degradation of 25 ppm naphthalene solution.

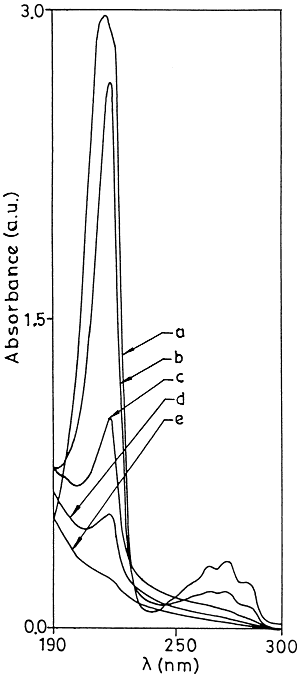


Fig. 6. Absorption spectra of 25 ppm naphthalene solution recorded at different time of light irradiation: (a) 0, (b) 10, (c) 25, (d) 40 and (e) 50 min.

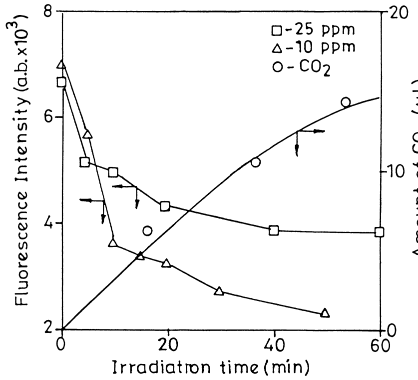


Fig. 7. Decrease in fluorescence intensity and formation of CO_2 of aqueous solution of anthracence during photocatalytic reaction.

the surface of the film shows textured uniform clusters of TiO_2 grains throughout the surface. At higher magnification, this shows highly porous sponge-like surface.

4. Photodegradation of naphthalene and anthracene

Saturated aqueous solution (about 10–25 mg/l) of naphthalene and anthracene was prepared by constant shaking of the volumetric flask for a long time, though this amount is not totally soluble in 1 l of water. This solution was regarded as 25 ppm solution of naphthalene and anthracene, respectively. A 50-ml (25 ppm) solution of these hydrocarbon and TiO_2 thin film sintered at 400°C, have been used for experimental purpose. At different time intervals, 5 ml reaction solution was withdrawn for the analysis. The analysis of naphthalene solution was done by measuring its absorbance at 275 nm, and the analysis of anthracene solution was done by measuring its fluorescence intensity at 400 nm using excitation wavelength of 254 nm. Fig. 5 shows the decrease in fluorescence intensity of 25 ppm naphthalene solution with illumination time. Around 15–25 μl of CO_2 was measured during the degradation of naphthalene as can be seen from Fig. 5. The concentration of naphthalene is almost reduced to zero after 50 min light illumination. The rate constant calculated from the slope of the plot log(abs) + 1 vs. time for 10 and 25 ppm solution are (0.0265 and 0.0479 min^{-1}, respectively) very high.

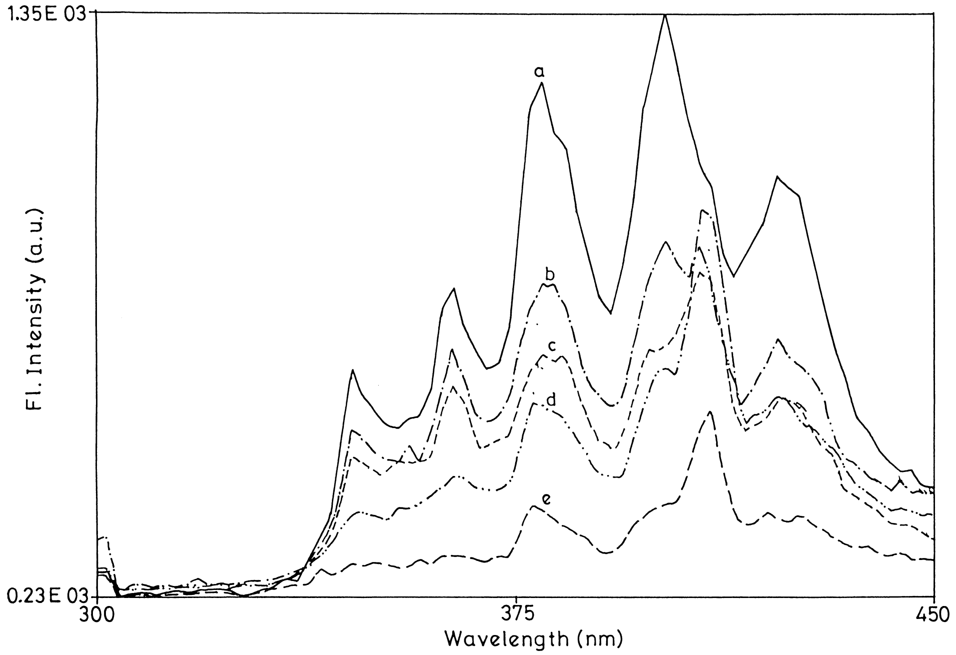


Fig. 8. Fluorescence spectra of anthracence solution recorded at various time of light irradiation over TiO_2 film: (a) 0, (b) 10, (c) 20, (d) 30 and (e) 50 min.

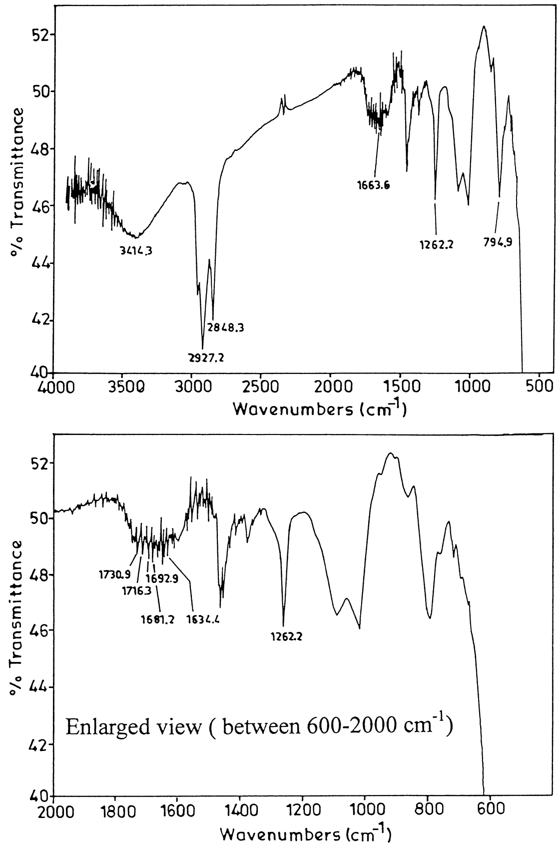


Fig. 9. FTIR spectra (neat) of the intermediates formed, during naphthalene solution degradation after 120 min of light irradiation over TiO_2 film.

Fig. 6 shows how the absorbance of aqueous solution of naphthalene gradually decreases with illumination time and ultimately levels off to zero after 50 min of UV light irradiation. Fig. 7 shows the change in fluorescence intensity and CO_2 formation during the decomposition process of aqueous solution of 10 and 25 ppm anthracene with irradiation time. There are abrupt changes in intensity at the initial time, which finally leveled off. One typical fluorescence spectrum of anthracene solution during the progress of the degradation reaction is shown in Fig. 8. The initial pH of the aqueous solution of these polyaromatic hydrocarbon was 6.65, which was changed to 5.92 after the mineralisation process. This pH change is mainly due to the formation of various intermediate photoproducts and also, to the release of H^+ ions in the solution. These intermediate photoproducts were identified by FTIR and GC-MS studies.

4.1. Identification of intermediate products

For identification of intermediates, the saturated aqueous solution of naphthalene and anthracene were irradiated over TiO_2 thin film for 2 h. The irradiated solution was then extracted with diethyl ether and was kept in dark overnight with Na_2SO_4 in order to remove any trace amount of water in the organic phase. The solvent was then evaporated with rotary evaporator. The residue was characterised by FTIR and GC-MS using HP-5 column. The FTIR spectra (neat, in CCl_4) are shown in Figs. 9 and

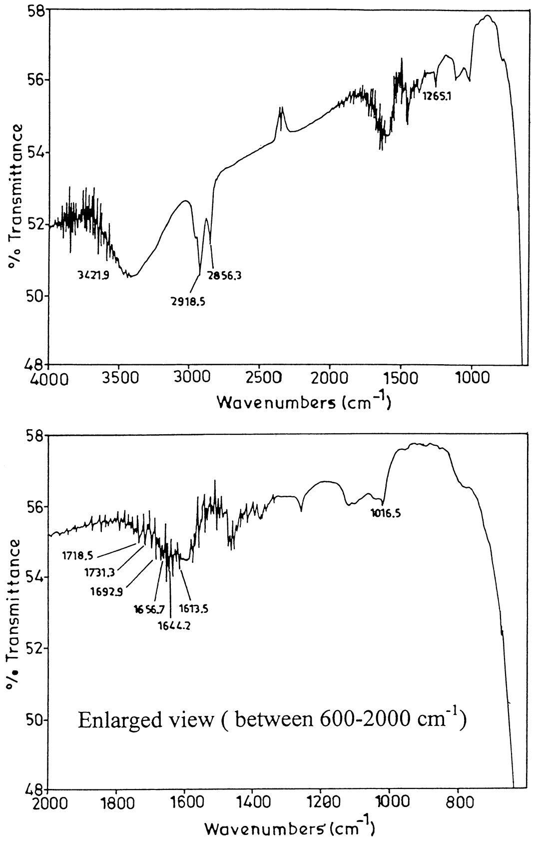
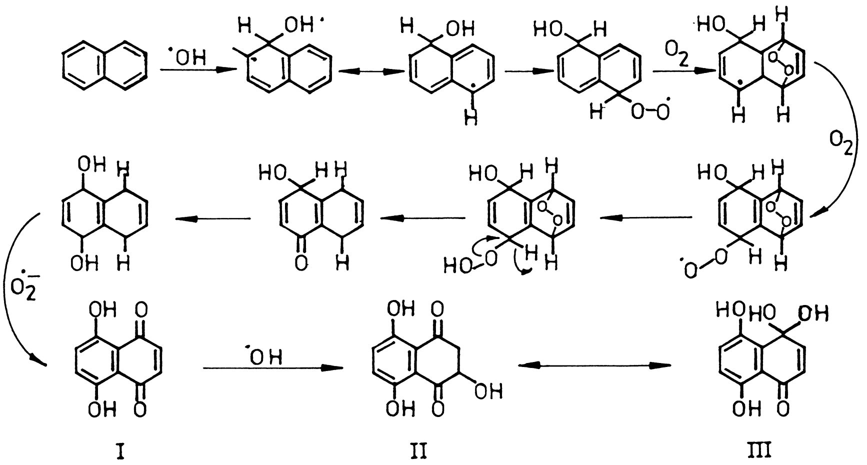
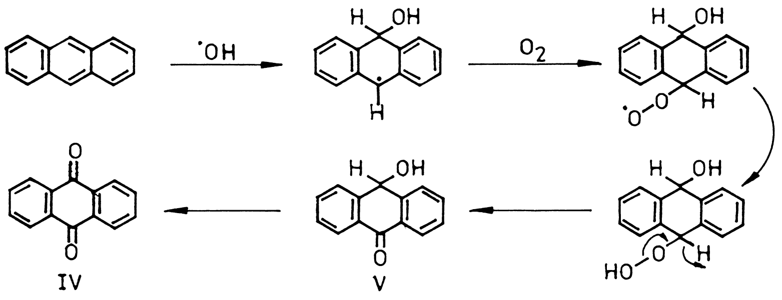


Fig. 10. FTIR spectra (neat) of the intermediates formed, during anthracence solution degradation after 120 min of light irradiation over TiO_2 film.



Scheme 1.

10. FTIR spectra displayed characteristic bands at 3414 cm^{-1} for OH groups, 2927 and 2848 cm^{-1} for CH stretching, 1716, 1692 and 1681 cm^{-1} for conjugated CO, and 1634 cm^{-1} for C=C aromatic, for naphthalene solution. Similarly, for anthracene solution, these are 3421 cm^{-1} for OH, 2918 and 2856 cm^{-1} for CH stretching, 1718 and 1692 cm^{-1} for conjugated CO, and 1613 cm^{-1} for C=C, aromatic. The mass spectra shows many fragmentation peaks. We are unable to characterise all *m/z* fragmentation value. Three most probable products were identified from the naphthalene degradation by matching their IR spectra and GC-MS analysis. These are 5,8-dihydroxy-1,4-naphthaquinone (I), 2,5,8-trihydroxy-2,3-dihydronaphthaquinone (II)



$$TiO_2 \xrightarrow{h\nu} e^- + h^+$$
$$H_2O \text{ or } {}^-OH + h^+ \longrightarrow H\dot{O} + H^+$$
$$O_2 + e^- \longrightarrow O_2^{\cdot-} \xrightarrow{H^+} H\dot{O}_2$$
$$2H\dot{O}_2 \longrightarrow H_2O_2 + O_2$$
$$H_2O_2 \xrightarrow{h\nu} 2\,{}^{\bullet}OH$$
$$H_2O_2 + e^- \longrightarrow OH + {}^-OH$$

Scheme 2.

and 4,4,5,8-tetrahydroxy anthraquinone (III) of equal mass. In the mass spectra, an m/z value of 191 corresponds to $M^{+}+1$ fragmentation of compound I of molecular weight 190 and an m/z value of 207 corresponds most probably to $M^{+}-1$ fragmentation of compounds II and III of molecular weight 208. Compound III is highly improbable because two hydroxyl groups are at the same carbon, which is unstable and must be converted to the corresponding keto form. Thus, the most probable intermediates of naphthalene degradation are compounds I and II. Similarly, in the case of anthracene degradation, two most probable intermediates were isolated by comparing the IR spectra. These are anthraquinone (IV) and 6-hydroxy anthraquinone (V). The compound (IV) was also confirmed by HPLC chromatogram using standard sample of anthraquinone. This is also further supported by other reports [19,25,26], where formation of phthalic acid, polyhydroxylated aromatic compounds and anthraquinone has been identified as the main intermediates. Based on the above discussions, a plausible reaction mechanism involving the hydroxyl and superoxide radicals for the possible formation of intermediates are discussed in Schemes 1 and 2. The major oxidation step is believed to be initiated by hydroxy radicals, which are generated following the oxidation of hydroxyl ions by photogenerated holes trapped at the TiO_2 surface.

5. Conclusion

The porous thin film of TiO_2 is highly efficient for the degradation of naphthalene and anthracene. The rate constants are high and the reactions mostly follow the first order kinetics. Mainly polyhydroxylated and carbonylated intermediates are formed, which are ultimately converted to carbon dioxide. The amount of CO_2 as the final mineralisation product has been measured in stoichiometric amount. Since the problem of total conversion to CO_2 is of considerable importance in any water decontamination process, the potentiality exists for the application of photocatalytic methods in the purification of water polluted by these polyaromatic hydrocarbons.

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