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Photocatalytic degradation of H-acid over a novel TiO_2 thin film fixed bed reactor and in aqueous suspensions☆

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Abstract

The present work is focused on the heterogeneous photocatalytic degradation of H-acid, a toxic and non-biodegradable dye intermediate, in TiO_2 suspensions and TiO_2 thin film fixed bed reactor (TFFBR). The degradation studies in slurry form are investigated using TiO_2 Degussa P25 and different Millennium PC50, PC100 and PC500 photocatalysts under UV illumination. The study includes dark adsorption experiments in different pH conditions, influence of the amount of photocatalyst, effect of H-acid concentration, effect of pH on chemical oxygen demand (COD), biological oxygen demand (BOD) and the sulfate ion formation during the photocatalytic degradation. Photocatalytic treatment significantly reduces COD and increases the biodegradability of H-acid. The intermediates have been identified by LCMS. The study with slurry is extended to the immobilization of preformed TiO_2 Degussa P25 in thin film using an acrylic emulsion by simple spray technique on inert Cuddapah stone. This method of immobilization does not require the thermal treatment of the catalyst at high temperatures. It may be used for the photocatalytic treatment of effluents at a higher scale.

Keywords: Solar irradiation; Photodegradation; H-acid; Immobilized TiO_2; Biodegradable

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1. Introduction

Dye and dye intermediates with high degree of aromaticity and low-biodegradability are introduced into the aquatic system results in the increase of the environmental risk. Conventional methods such as biological, physical and chemical processes are having several drawbacks and they are not effective for complete degradation of recalcitrant organic compounds [1]. The development of alternative methods able to degrade toxic organic compounds is necessary. In this regard advanced oxidation processes (AOP) have attracted a great attention. Heterogeneous photocatalysis mediated by TiO_2 is of considerable interest for the wastewater treatment. Many semiconductors like TiO_2, ZnO, CdS, etc., have been employed as photocatalysts. As generally observed TiO_2 is an efficient photocatalyst with high quantum yields. Photocatalysis by TiO_2 ($E_g = 3.2\,eV$) involves under UV light excitation the generation of e^- and h^+ in conduction band and in the valence band, respectively. These species undergo charge transfer reactions across the interface with the oxygen, water or organic pollutants adsorbed on TiO_2 surface. The reaction of h^+ with OH^- or H_2O leads to the generation of reactive $^{\bullet}OH$ radicals which are powerful oxidants attacking the recalcitrant organic compounds of interest [2–9].

Most of the studies related to photodegradation have been carried out using the suspension of powder TiO_2 in aqueous solutions. However, the use of aqueous suspension is limited for practical application by filtration problems due to the small size of TiO_2 particles. Alternatively, the catalyst may be immobilized on to a suitable solid inert support, which eliminates the need of removing the catalyst. Unfortunately, when the catalyst is immobilized there is a decrease in the available surface area for the reaction since the catalyst must adhere to the solid support and the reactor design is limited by the optical absorption constraints.

Many techniques were proposed for the immobilization of TiO_2 on solid supports like glass [9], quartz [10], silica, activated carbon [11], fiberglass cloth, zeolites [12] and stainless steel, etc. Mikula et al. [14] reported the immobilization of TiO_2 (P25) on fiberglass and slurry forms show

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comparable activities for the photocatalytic transformation of phenol. However, supporting TiO_2 is commonly reported to be less photoactive. Generally, the process of immobilization involves the use of expensive precursors of TiO_2 in the form of sol–gel and a thermal treatment of the film between 400 and 500 °C. Zeolites based photocatalysis is new and the work reported involves the use of high TiO_2 loading. However, very recently Durga Kumari et al. [13] reported that the dispersions of TiO_2 on zeolite enhance the photocatalytic properties.

H-acid (4-amino-5-hydroxy-2,7-naphthalene disulfonic acid monosodium salt) is an important dye intermediate and its presence is significant in effluents of dye industries existing in Hyderabad. Because of its high toxicity and hydrophilicity, H-acid is extremely difficult to eliminate. Earlier communication from Yu et al. [15] reported that 90% of H-acid was degraded during 5 h illumination over Degussa P25 TiO_2. They showed that the degradation rate is enhanced by the presence of inorganic oxidants like Ag^+/Fe^{3+}, but their study is limited to the disappearance of H-acid.

The present investigation highlights the photocatalytic degradation of H-acid in suspensions of Degussa P25 TiO_2 and on various Millennium TiO_2 photocatalysts. The influence of various operational parameters like the amount of catalyst, the concentration of H-acid and pH of the solution, on the adsorption properties of the acid, COD, BOD and sulfate ion generation are studied. Some of the intermediate products formed during photocatalytic degradation process are identified. Furthermore, the study is planned a method to immobilize commercially available TiO_2 powder (Degussa P25) in the form of a film, using an acrylic emulsion by spray technique or simply spread with a brush on a solid support like Cuddapah stone from Andhra Pradesh (India). Immobilized TiO_2 film in the form a thin film fixed bed reactor (TFFBR) was used to study the degradation of H-acid.

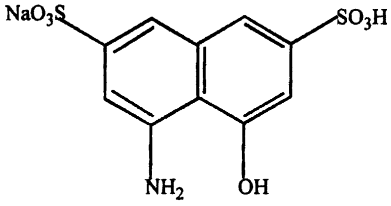
2. Experimental

2.1. Materials

Titanium dioxide Degussa P25 and TiO_2 Millennium Inorganic Chemicals that are denoted as Millennium PC50, PC100 and PC500, were used and their physical properties are listed in Table 1. H-acid (4-amino-5-hydroxy-2,7-naphthalene disulfonic acid monosodium salt) was from Aldrich (structure given below) and used as received. Acrylic emulsion (with percentage of solids of 55 ± 1 and viscosity of 4–10 Poise; pH 7–9; percent free monomer <0.5; particle size by SEM: 0.3–0.5 nm; MFT: 20–25 °C). All the solutions were prepared with de-ionized water.

Table 1
Physical characteristics of the TiO_2 catalysts

Origin	Type	Composition	Size of crystallites (nm)	Surface area ($m^2\,g^{-1}$)
Degussa	P25	Anatase/rutile (70/30)	30	55 ± 15
Millennium	PC50	Anatase	20–30	45 ± 5
Millennium	PC100	Anatase	15–25	80–100
Millennium	PC500	Anatase	5–10	>250



Structure of H-acid

2.2. Analytical techniques

UV-Vis DRS of films were recorded on Cintra 10 spectrometer. The TiO_2 thin films were observed in Hitachi S-520 Scanning Electron Microscope. The COD measurements were performed using a HACH COD meter and BOD parameters were analyzed by measuring dissolved oxygen with a DO probe YS1 (5010, USA) instrument. The samples were kept in BOD incubator for 5 days at 20 °C. Sulfate ion concentration was quantified spectrophotometrically at 420 nm using a CECIL 2021 spectrophotometer, at the end of each illumination experiments [16].

The formation of intermediates during the degradation of the salt was monitored by HPLC using a C-18 column and methanol/water ratio of 70/30% (v/v) as mobile phase with a flow of 1 ml min^{-1} and the intermediate products were identified by LCMS.

2.3. Adsorption experiments—TiO_2 suspensions

Prior to the start of the photocatalytic experiments, adsorption (dark) experiments were done. The adsorption was investigated initially with the H-acid solution (pH ∼ 5) and at pH 2 and 10 (adjusted with HCl and NaOH) on different TiO_2 catalysts and the percent adsorption of solutions were monitored. An amount of 30 mg of TiO_2 was used in all the adsorption experiments using 10 ml of H-acid (1.46×10^{-4} M) solution. The samples were left overnight in dark with stirring to reach the adsorption equilibrium on the surface of the catalyst and then filtered. The extent of the adsorptions was determined from the decrease in the H-acid solution concentration [17].

2.4. Photocatalytic experiments—TiO_2 suspensions

Photolysis experiments were carried out in 100 ml quartz reactor illuminated with 250 W mercury lamp. In a typical experiment a known concentration of H-acid, 50 ml (1.46×10^{-4} M) and TiO_2 were kept under continuous stirring. Prior to the start of irradiations, the adsorption studies

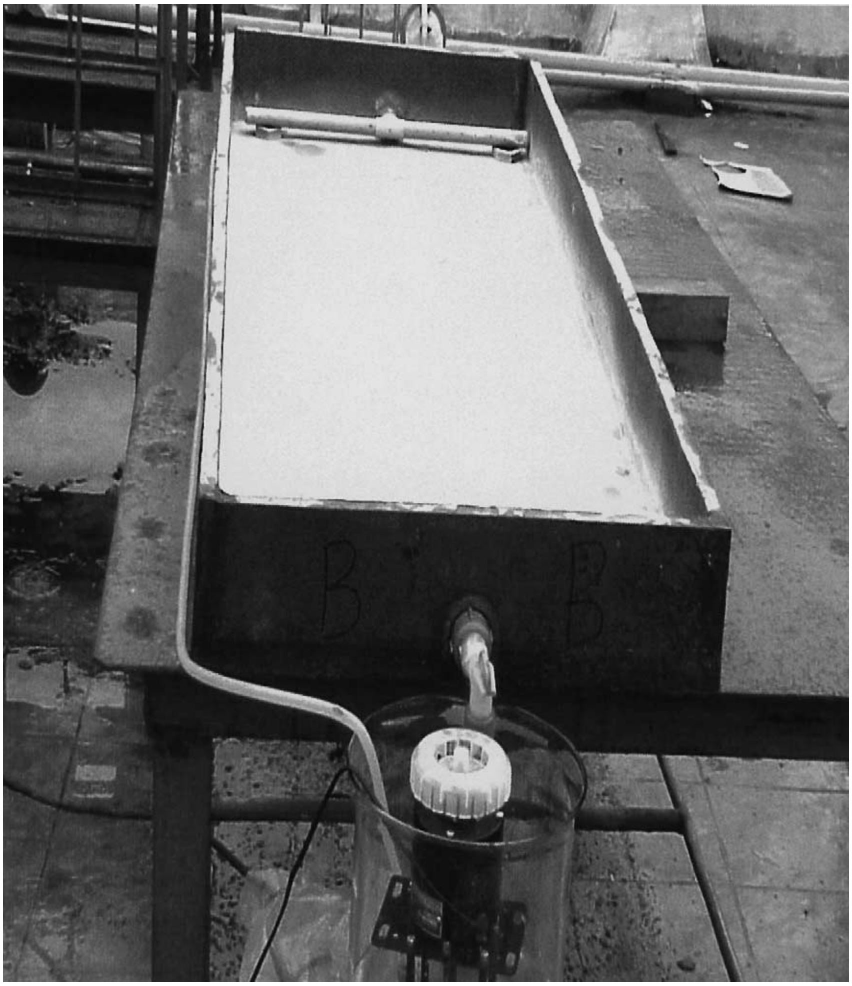


Fig. 1. Photograph of TiO_2 TFFBR. Size: 144 cm × 52 cm × 10 cm; solution flow rate: 750 ml min^{-1}; batch size: 5 l.

(dark) were done for all the catalysts for 30 min. The photocatalytic experiments were monitored for 5 h and the samples were collected at regular intervals of time and filtered with syringe filters (0.20 μm) and the concentration changes of the H-acid solution were measured with UV absorption spectrophotometer (Cintra 5). The remaining part of the sample is used for the measurements of COD, BOD, etc.

2.5. *Preparation of TiO_2 TFFBR*

A TFFBR was made of Cuddapah stone (size: $l = 144$ cm; $b = 52$ cm and $h = 10$ cm). It is an inert solid support for the immobilization of TiO_2. The TiO_2 is suspended in minimum amount of water (4 g of TiO_2 in 100 ml of water) and 5 ml of acrylic emulsion is added under stirring. After cleaning the stone, the TiO_2 + acrylic emulsion mixture was spread with a laboratory spray gun. The coated TiO_2 film was left for air-drying. Coating was repeated twice to get an uniform film without pin holes.

The H-acid (10^{-4} M) solution of 5 l is continuously run through the reactor at the flow rate of 750 ml min^{-1} using circulation pump. The degradation experiments were monitored under solar illumination. A partial view of the thin film fixed bed photocatalytic reactor (Fig. 1).

3. Results and discussion

3.1. *Characterization of TiO_2 thin film*

3.1.1. *Scanning electron micrographs (SEM)*

The thin films of TiO_2 prepared by spray technique were analyzed by SEM. Fig. 2 shows the SEM of emulsion bound TiO_2 thin films: (a) emulsion film; (b) before use; and (c) after 30 days of use. From the micrographs it is observed that the TiO_2 is present on the surface of the film and that the emulsion matrix does not cover it. The emulsion matrix improves the adherence of the photocatalyst that is necessary to obtain a good photocatalytic activity. TiO_2 (white spots in Fig. 2(b) and (c)) is still present on the films even after continuous use for 30 days. The film is showing good abrasion resistance

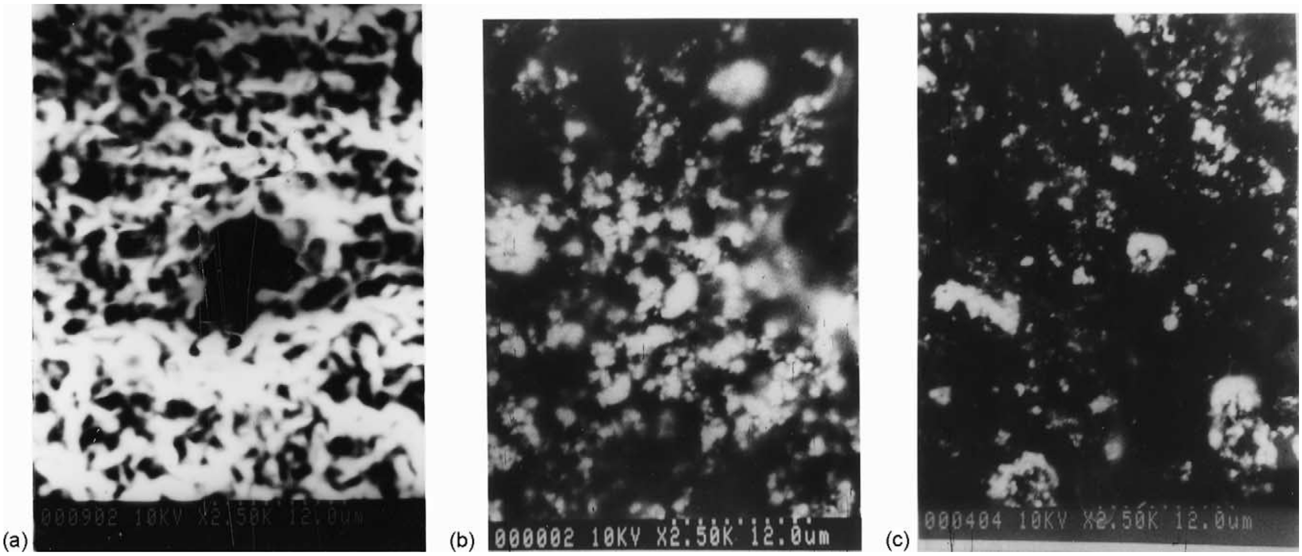


Fig. 2. SEM images of TiO_2 thin films supported on Cuddapah stone: (a) emulsion film (without TiO_2); (b) TiO_2 + emulsion film (before treatment); (c) TiO_2 + emulsion film (after 30 days treatment).

confirming the stability and good adherence even on continuous use.

3.1.2. *Diffuse reflectance spectra (DRS)*

In order to check the role of emulsion and its interaction with the film if any, the DRS of TiO_2 films were recorded. The DRS of the films shows no shift in the band gap of the TiO_2 after immobilization (Fig. 3). Thus the TiO_2 does not interact with the emulsion which is just used as an adhesive for holding the catalyst intact and enhancing the strength of the film.

3.2. *H-acid degradation—TiO_2 suspension*

3.2.1. *Effect of pH on H-acid adsorption (dark experiment)*

The semiconductor oxide particles are generally amphoteric in nature and the photocatalytic process takes place on the surface of TiO_2. The pH of the solution shows strong influences on the surface properties of TiO_2 particle. In order to investigate the effect of pH on the adsorption of H-acid over different catalysts, experiments were performed at pH ~ 5 (free pH of H-acid solution) pH 2 and 10, and the percent adsorption with the corresponding pH is plotted in Fig. 4. It is observed that the percent adsorption increases in acidic medium and decreases in basic pH. The same trend was observed for all the TiO_2 catalysts. P25 shows a greater adsorption of H-acid than Millennium TiO_2 catalysts. The strong influence of pH on the adsorption of H-acid depends on the specific nature of TiO_2 surface and it may be due to the intrinsic behavior of TiO_2 particle (isoelectric point at pH 4.3–6.4) [18] and also the nature of the H-acid. As H-acid has two negatively charged sulfonic groups, it is expected that at low pH, attractive forces are developed between substrate and TiO_2 surface, resulting in high adsorption in acidic medium. As the pH increases ($pH > 6.4$), TiO_2 surface is negatively charged, resulting in repulsive forces between the substrate and TiO_2 surface thus decreasing adsorption [17,19].

3.2.2. *Photocatalytic degradation of H-acid—suspensions of TiO_2 Degussa P25 and Millennium PC50, PC100, PC500 (light experiment)*

Photolysis experiments show 10–12% decrease in the H-acid concentration after 5 h of UV illumination as shown in Fig. 5. The photocatalytic degradation of H-acid over P25 TiO_2 is compared with Millennium TiO_2 photocatalysts, with an amount of $3\,g\,l^{-1}$. Adsorption (dark) experiments were carried out for all the catalysts. The results show greater adsorption on P25 TiO_2 compared to Millennium catalysts. In contrast, faster photocatalytic degradation rate is observed for PC500 compared to P25 TiO_2. Furthermore, PC100 shows slow rate of degradation among the Millennium catalysts. It is well known that for a photocatalytic process, adsorption properties of a photocatalyst play an important role during the degradation process and that the TiO_2 assisted photodegradation occur on or near, the semiconductor surface. In view of this, further experiments were carried out over Degussa P25 TiO_2 as a model photocatalyst.

3.2.3. *Influence of the amount of titania in suspension*

Photocatalytic degradation of H-acid may depend on the catalyst amount. In order to investigate the effect of catalyst amount on the percent degradation, experiments were performed over P25 TiO_2. It is seen that with increase in the amount of TiO_2 up to $3\,g\,l^{-1}$ there is an increase in the percent degradation and above which there is no much improvement in the degradation of the H-acid with an increase

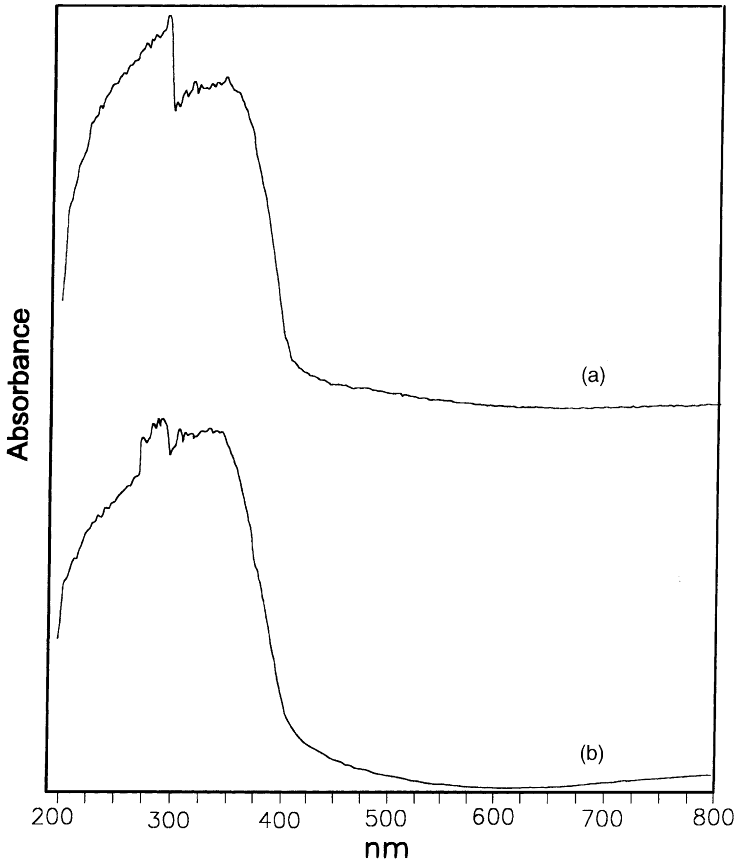


Fig. 3. UV-Vis DRS absorbance spectra of TiO_2 thin film: (a) before use; (b) after effluent treatment for 30 days.

in the catalyst amount as is shown in Fig. 6. It is observed that H-acid degradation is faster on TiO_2 at $3\,g\,l^{-1}$. For higher TiO_2 amount the rate of degradation is reduced due to the shielding effect of the suspended TiO_2 particles hindering the penetration of light [17,19]. The optimum amount of $3\,g\,l^{-1}$ is in good agreement with results previously reported [15]. All other series of experiments were carried using $3\,g\,l^{-1}$ of TiO_2.

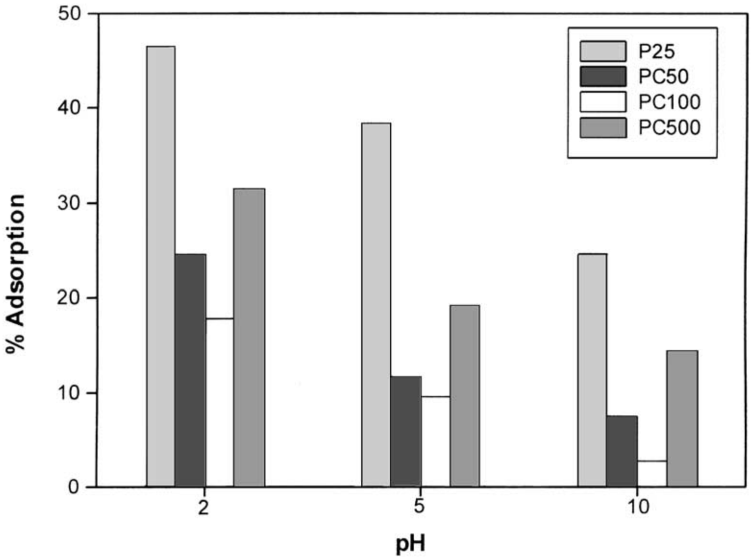


Fig. 4. Effect of pH on H-acid (10^{-4} M) adsorption over different TiO_2 photocatalysts ($3\,g\,l^{-1}$).

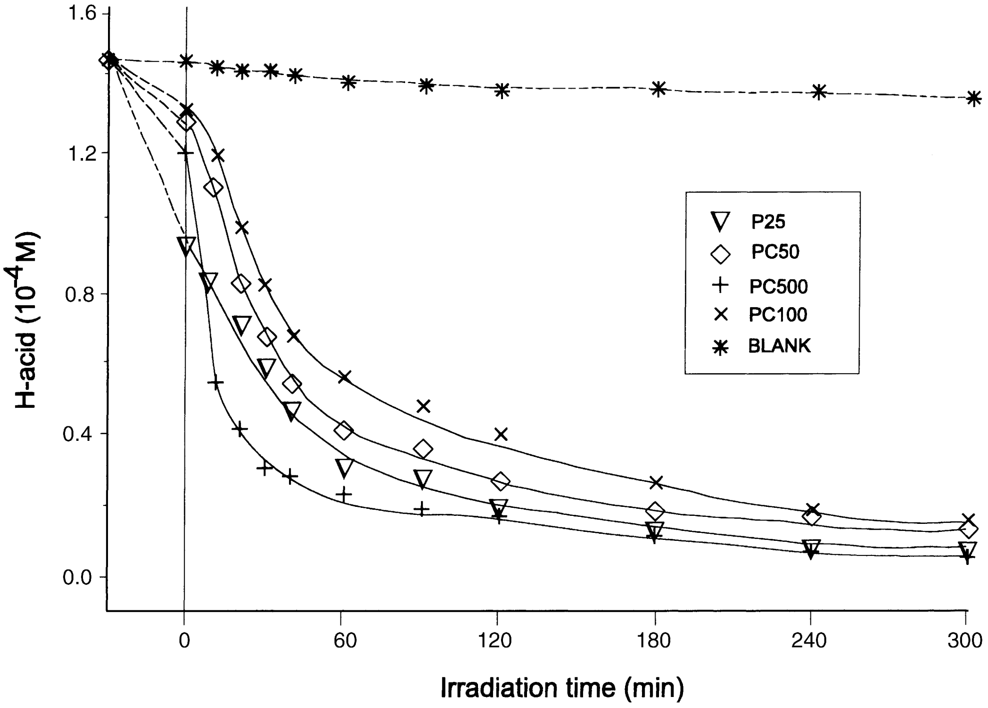


Fig. 5. Time dependence photocatalytic degradation of H-acid (10^{-4} M) over different TiO_2 catalysts ($3\,g\,l^{-1}$).

3.2.4. COD and BOD of degraded H-acid—TiO_2 suspensions

The influence of H-acid concentration on percent COD removal over P25 TiO_2 is shown in Fig. 7. It is seen clearly from the figure that the percentage of COD reduction decreases with increasing concentration of H-acid for the same irradiation time. Thus higher concentrations of H-acid may need longer illumination time.

The studies were extended to the effect of pH on the COD and BOD levels in P25 TiO_2 suspensions as shown in Fig. 8.

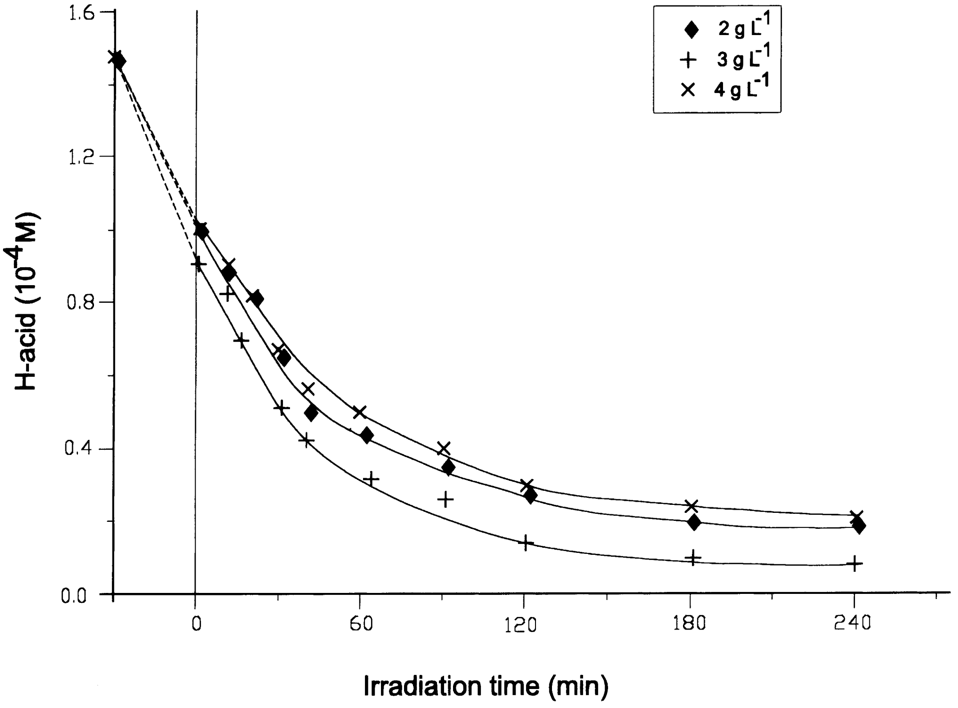


Fig. 6. Effect of photocatalyst amount (P25 TiO_2) on the degradation of H-acid (10^{-4} M) with illumination time.

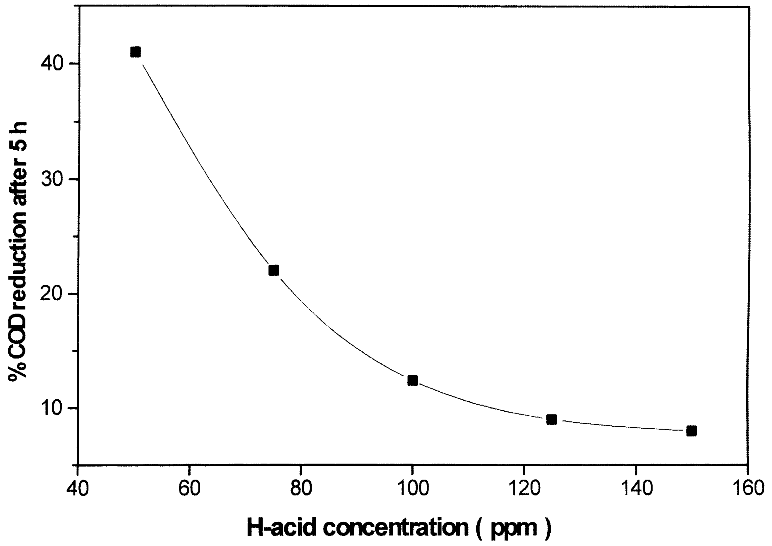


Fig. 7. Effect of H-acid concentration on percent COD reduction after 5 h UV irradiation over Degussa P25 TiO_2 ($3\,g\,l^{-1}$).

It appears that the photocatalytic degradation is faster at pH ∼ 5 (pH of H-acid solution). In highly acidic as well as in basic media there is a low degradation of H-acid. Thus, the pH 4–8 is the best range for the effective photocatalytic degradation of H-acid. The TiO_2 mediated photocatalytic process considerably decreased the COD by 41% and there is a substantial increase in the BOD values. These features imply that the photocatalytic process enhances biodegradability.

The effective degradation was confirmed by the formation of sulfate ion concentration in solution with time. The sulfate ion formation at pH ∼ 5 is maximum and it is minimum at pH 2 and 10 as is shown in Fig. 8. The formation of sulfate ion is a proof of the degradation of organic moiety by the attack of hydroxyl radical [20].

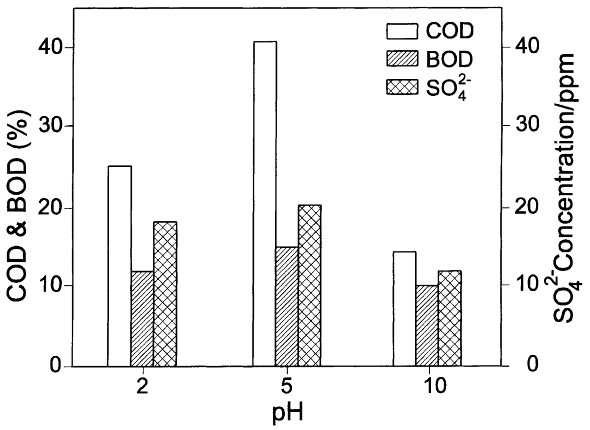


Fig. 8. Effect of pH on variation of percent COD decrease and BOD increase and the formation of sulfate ion (ppm). Initial H-acid concentration (10^{-4} M); P25 TiO_2 ($3\,g\,l^{-1}$); illumination time: 5 h.

3.3. H-acid degradation—TFFBR

The degradation of H-acid on immobilized TiO_2 (TFFBR) was monitored under solar illumination for 3 days. H-acid of 10^{-4} M solution was run through the TFFBR of area 7488 cm^2 at a flow rate of 750 ml min^{-1}. To compensate the concentration due to evaporation, water is added at regular intervals. The samples collected at the end of experiment were analyzed for the COD and BOD values in order to evaluate the extent of biodegradability of H-acid. COD removal was 62% and there was an increase of BOD at the end of third day of solar photocatalytic experiments as shown in Table 2.

3.4. Post-characterization of thin films

In the method developed for the immobilization of TiO_2 the adherence of TiO_2 is improved by using the acrylic emulsion. On drying, the emulsion binds to the support surface and forms a matrix like network that maintains TiO_2 particles without affecting their photocatalytic activity. The TFFBR was used continuously in order to test the strength of the film, it was noted that at the end of 30 days of treatment, the film was intact and the activity of TiO_2 remained almost unchanged. Then the film was analyzed by SEM and

Table 2
Photocatalytic degradation of H-acid over TiO_2 suspension (using UV light) and TiO_2 thin film over Cuddapah stone (using solar illumination)

Parameters	TiO_2 suspension irradiation time: 5 h	TiO_2 film irradiation time: 15 h (3 days)
Percentage of degradation	100	100
Percentage of COD removal	41	62
Percentage of BOD increase	15	18

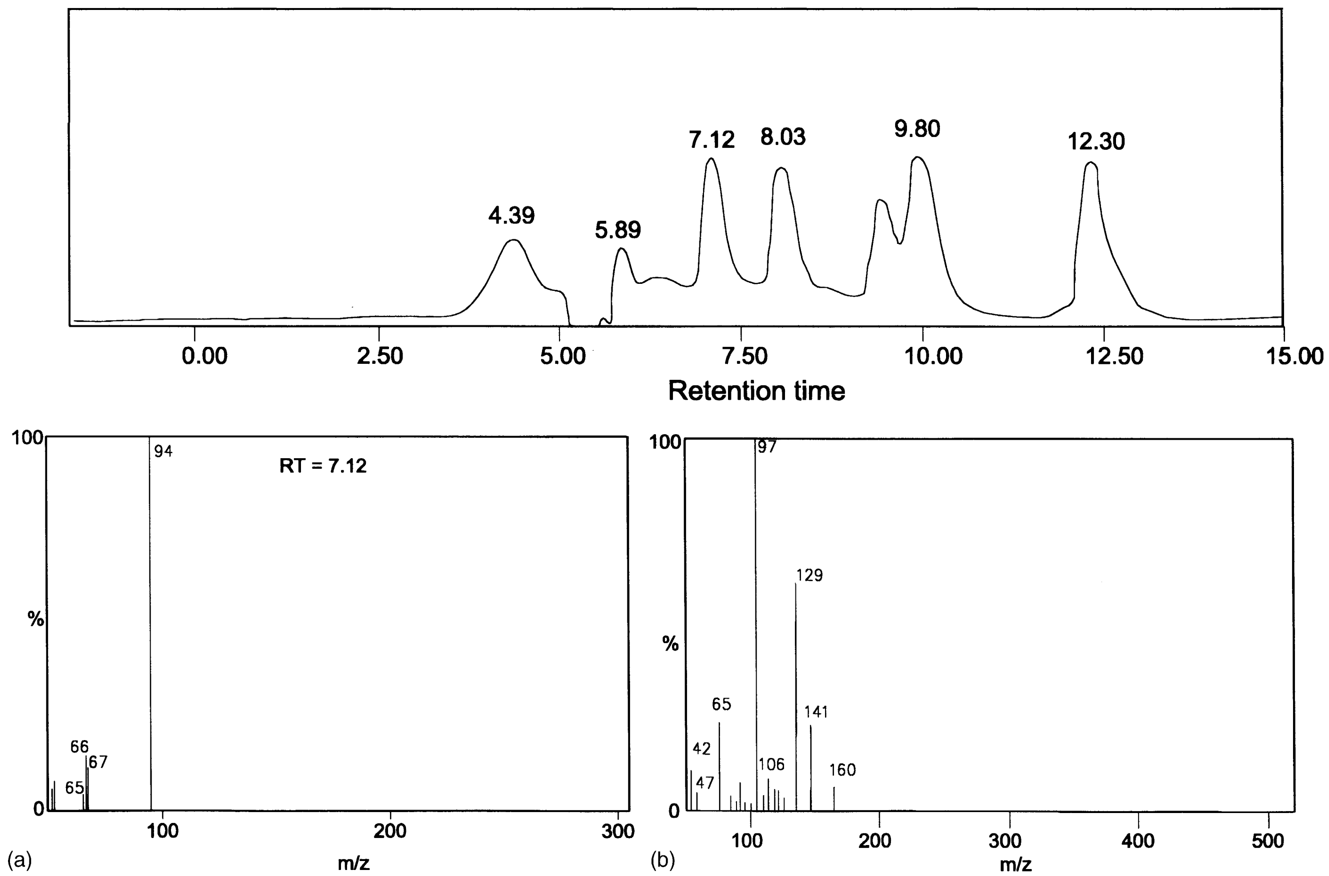


Fig. 9. LC-chromatogram of the H-acid degradation and LCMS of: (a) phenol; (b) unidentified product obtained on photocatalytic degradation of H-acid.

DRS. The presence of TiO_2 on the surface of emulsion matrix is as shown in Figs. 2(c) and 3(b). The immobilization of TiO_2 using the emulsion does not bring any interaction between TiO_2 and the emulsion matrix, since the preparation of the film involves only a physical mixing. It may be noted from DRS spectra of the films that there is no shift in the band gap of emulsion bound TiO_2.

3.5. Degradation pathway

In the present study some intermediates formed during the photocatalytic degradation have been identified. Experiments were carried out with UV light using titania Degussa P25 as a reference photocatalyst. The oxidizing hydroxyl radical attacks at the aromatic ring leads to the formation of hydroxylated intermediates. Furthermore, on repeated photooxidation a decrease in the aromaticity. Phenol ($m/z = 94$), benzoquinone ($m/z = 108$) were identified from LCMS. The value $m/z = 122$ was tentatively attributed to benzoic acid. The mass spectrum of another product was obtained but not identified (Fig. 9). These products result from the elimination of sulfonyl group and a multistep oxidation of one aromatic ring. The oxidative photodegradation of H-acid involves several intermediates and it is very difficult to identify all of them, as it is known that radical induced reaction processes involves number of intermediates at very low concentrations.

3.6. Transformation of slurry reactor of lower scale to TFFBR of higher scale

TiO_2 suspension	TiO_2 immobilized (TFFBR)
Slurry reactor	Fixed bed reactor
$3\,g\,TiO_2\,l^{-1}$	$4\,g\,TiO_2\,5\,l^{-1}$ (used for thin film)
Batch size: 50 ml of H-acid (10^{-4} M)	Batch size: 5000 ml of H-acid (10^{-4} M)
Source of illumination: UV light	Source of illumination: solar light
Time of treatment: 5 h	Time of treatment: 15 h (3 days)
Decrease in COD is ~41%	Decrease in COD is ~62%
Separation of photocatalyst required	Separation of photocatalyst not required
Catalyst is reused after separation and washing	Film is reused after washing
Batch process	Continuous process

4. Conclusion

P25 TiO_2 is an effective photocatalyst for the degradation of H-acid. The optimal amount of TiO_2 for the effective photocatalytic degradation of H-acid is $3\,g\,l^{-1}$ in slurry form. The degradation of H-acid is associated with the generation of sulfate ion. From the adsorption experiments in suspension, it is noteworthy that H-acid interacts more with TiO_2 in acidic than in basic medium. In the photocatalytic degradation of H-acid there is a considerable decrease in COD values and an increase in BOD values that proves the reduction in the toxicity of the H-acid thus increasing the biodegradability of the intermediates formed during the photocatalytic degradation.

The degradation of H-acid on an immobilized TFFBR is a useful method for the degradation of organic recalcitrant pollutants since it avoids the post-treatment filtration. The method adopted for the immobilization involves the preformed TiO_2 and does not require expensive precursors. Photocatalytic films are easily drawn by spray technique and used without any heat treatment. The present results suggest that TiO_2 photocatalyst in such an immobilized form is economical and efficient process for the treatment of effluents at larger scale that may be adopted for diluted wastewaters containing H-acid. The application of the present TFFBR for the treatment of other industrial pollutants is also in progress.

Acknowledgements

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References

[1] A. Houas, H. Lachheb, M. Ksibi, E. Elaloui, C. Guillard, J.M. Herrmann, Appl. Catal. B 31 (2001) 145–157 (and references therein).

[2] D.M. Blake, Bibliography of Work on Photocatalytic Removal of Hazardous Compounds from Water and Air, NREL/TP-430-22197, National Renewable Energy Laboratory, Golden, Co, 1999.

[3] K.V. Subba Rao, D. Venu Gopal, M. Subrahmanyam, Ind. J. Chem. 38A (1999) 173–175.

[4] A. Rachel, M. Sarakha, M. Subrahmanyam, P. Boule, Appl. Catal. B 37 (2002) 293–300.

[5] A. Rachel, M. Subrahmanyam, P. Boule, Appl. Catal. B 37 (2002) 301–308.

[6] A. Rachel, B. Lavédrine, M. Subrahmanyam, P. Boule, Catal. Commun. 3 (2002) 165–171.

[7] V. Madhuri, M. Noorjahan, V. Durga Kumari, M. Subrahmanyam, P. Boule, Proceedings of the International Conference on Materials for Advanced Technologies, Singapore, July 2001, p. 261.

[8] M. Subrahmanyam, K.V. Subba Rao, M. Rajesh Babu, B. Srinivas, Ind. J. Environ. Protect. 18 (1998) 266–272.

[9] R.L. Pozo, M.A. Batanas, A.E. Cassano, Catal. Today 39 (1997) 219–231.

[10] J.M. Herrmann, H. Tahiri, Y. Ait-Ichou, G. Lassaletta, A.R. Gonzalez-Elipe, A. Fernandez, Appl. Catal. B 13 (1997) 219–231.

[11] T. Torimoto, Y. Okawa, N. Takeda, H. Yoneyama, J. Photochem. Photobiol. A 103 (1997) 153–157.

[12] S. Horikoshi, N. Watanabe, H. Onishi, H. Hidaka, N. Serpone, Appl. Catal. B 37 (2002) 117–129.

[13] V. Durga Kumari, M. Subrahmanyam, K.V. Subba Rao, A. Ratnamala, M. Noorjahan, K. Tanaka, Appl. Catal. A 234 (2002) 155–165.

[14] M. Mikula, V. Brezova, L. Ceppan, L. Puchg, L. Karpinsky, J. Mater. Sci. Lett. 14 (1995) 615–616.

[15] G. Yu, W. Zhu, Z. Yang, Z. Li, Chemosphere 36 (1998) 2673–2681.

[16] Standard Methods for the Examination of Water and Wastewater, 18th ed., APHA, Washington, USA, 1992.

[17] F. Kiriakidou, D.I. Kondarides, X.E. Verykios, Catal. Today 54 (1999) 119–130.

[18] K. Tanaka, K. Padermpole, T. Hisanaga, Water. Res. 34 (2000) 327–333.

[19] F. Zhang, J. Zhao, T. Shen, H. Hidaka, E. Pelizzetti, N. Serpone, Appl. Catal. B 15 (1998) 147–156.

[20] B. Sangchakr, T. Hisanaga, K. Tanaka, J. Photochem. Photobiol. A 85 (1995) 187–190.