

Solar photocatalytic treatment of gelatin industry effluent: Performance of pilot scale reactor with suspended TiO₂ and supported TiO₂

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Degradation of gelatin in the effluent by heterogeneous photocatalysis using suspended and supported TiO₂ in falling film photoreactor under natural solar light has been investigated. Suitable weight proportions of slurry comprising fevicol and home-made TiO₂ have been prepared and the fevicol TiO₂ (F-T) film on acrylic sheet is obtained by brush coating. TiO₂ coating containing 10 wt% fevicol is found to be more adherent and efficient for gelatin degradation. This F-T catalyst in the falling film photoreactor has been tested for the treatment of effluent and its efficiency is compared with suspended homemade TiO₂. The effects of operational parameters such as the amount of TiO₂, effluent concentration, and initial pH on treatment process by F-T coating as well as by suspended TiO₂ slurry have been analyzed. The F-T film is efficient for repeated treatment of effluent when compared to suspended TiO₂. Hence this cost effective solar photocatalytic process is widely applicable at industrial scale.

Keywords: Suspended TiO₂, Falling film photoreactor, Solar light, Gelatin industry effluent, Degradation, Photocatalysis

Nowadays surface waters receive large amounts of varied domestic and industrial wastes. These water sources when used for agricultural irrigation, domestic consumption, leisure activities, etc, can be hazardous to the human health and to the environment¹⁻³. Gelatin is a protein substance that is extracted from collagen, a natural protein present in skin, bones, and animal tissue. As a protein, it has various applications and particularly used in the manufacture of medicinal capsules. The gelatin manufacturing process primarily involves selective hydrolysis and extraction of collagen from the connective tissues of animals. In India, the conventional raw materials used in the gelatin production are bovine bones. The effluent is generated in the processing sections where raw materials are cleaned, and in washing of process materials and the equipments used in the manufacture of gelatin. This wastewater contains lipids, which create a high biological oxygen demand (BOD).

Maree *et al.*⁴ reported that the effluents from gelatin manufacturing industry possess high pH, COD, calcium content and bad odour. Conventionally these

type of effluents are biologically treated using the activated sludge method based effluent treatment plants (ETP)⁵. But the disposal of organically rich sludge generated from these ETPs requires a large dump yard and this sludge may potentially cause environmental pollution by leaching or harboring pathogens. Furthermore lipid materials in these effluents cannot be completely biodegraded by the conventional biological wastewater treatment processes.

Solar photocatalytic oxidation is an attractive alternative process since it uses sunlight as the irradiation source and there is proven mineralization of a wide range of toxic organic contaminants⁶⁻¹⁰. There are many successful solar pilot scale processes reported using TiO₂ suspensions for wastewater treatment^{2,11,12} but many of them suffer from an inherent catalyst separation problem that may present a significant hurdle to commercial application. Solar fixed bed photocatalysis overcomes any need for separation and is receiving increasing interest as a low energy alternative for the treatment of industrial effluent.

Though a number of techniques such as sputtering¹³ and evaporation¹⁴ for the deposition of TiO₂ are available, they are expensive. Therefore, sol-gel process based dip-coating, spray coating and brush painting with appropriate catalyst binder compositions can be considered more practical and economical¹⁵. Hence, an attempt was made to reinforce TiO₂ film by introducing an adhesive Fevicol into slurry that may interlace and strengthen the coating.

In continuation of our work on solar energy utilization for toxic chemical degradation in a bench scale solar reactor^{7,9,16,17}, we present the degradation of gelatin industry effluent with Fevicol TiO₂ film on falling film reactor using direct sunlight. To the best of our knowledge, the use of poly synthetic resin Fevicol TiO₂ film over hydrophobic surfaces such as acrylic plastic has not been reported earlier for the treatment of effluent.

Experimental Section

Material

Fevicol was used as binder between the TiO₂ and the acrylic sheet, (3 mm thick) (Pidilite Industries Ltd, India). ZnO (Merck) has a particle size of 0.1-4 μm with the surface area 5 m²g⁻¹. A gift sample of Degussa TiO₂-P25 was obtained from Evonik (Germany). It is a 80:20 mixture of anatase and rutile with the particle size of 30 nm and BET specific area of 50 m²g⁻¹. AnalaR grade tetraisopropyl orthotitanate (Himedia, 98.0%), 2-propanol (99.5%, Spectrochem) ethanol (E-Merck) were used as received. The pH of the solutions was adjusted using H₂SO₄ or NaOH.

Wastewater sample was taken from an industry located in SIPCOT complex Semmankuppam, Cuddalore, Tamil Nadu (India) which is manufacturing Ossein, Di Calcium Phosphate (DCP) and Gelatin from animal bones.

Preparation of home made TiO₂

Homemade TiO₂ was obtained by sol-gel method. Tetraisopropyl orthotitanate (12.5 mL) was dissolved in 100 mL of 2-propanol (Spectrochem P 99.5%) and to this solution 3 mL of water was added drop wise under vigorous stirring. The resulting colloidal suspension was stirred for 4 h. The gel obtained was filtered, washed and dried in an air oven at 100°C for 5 h. The sample was calcinated at 400°C in a muffle furnace for 12 h to get TiO₂.

Coating Method

The requisite amount of the Fevicol (viz. 5, 10, 15, and 25 wt% with respect to the weight of TiO₂) and

TiO₂ in water were taken in a beaker and continuously stirred in a mechanical stirrer for 20 min to get a paste. This smooth paste of Fevicol-TiO₂ was coated on the surface of acrylic sheet using a soft 2 inch brush. Prior to this, the surface of the sheet was made rough by abrading with a sand paper. The sand blasting of acrylic plastic sheet was carried out unidirectional along the length. The coated acrylic sheet was dried at ambient temperature and the procedure was repeated till a uniform coating was obtained. The Fevicol-TiO₂ film (F-T film) dried completely for one day at room temperature.

Falling film reactor (FFR)

Falling film reactor (FFR) fabricated in our laboratory is shown in Fig. 1. The photoreactor has 3 mm thick acrylic plastic sheet. The photocatalyst is coated on acrylic sheet and it is mounted on a fixed platform inclined at 37° angle for maximum irradiation. The available geometric area of the acrylic transparent sheet (length, 1.13 m, breadth, 0.375 m) is approximately 0.43 m². The reactor is provided with inlet and outlet nozzles. Effluent is allowed to fall in a small tank at top with steel rollers and it is made to flow evenly as a film, over catalyst coated surface through the holes and it is collected at the bottom through the outlet. The reactor was operated in a circulation mode using a peristaltic pump.

Analysis

All photocatalytic experiments were carried out under similar conditions on sunny days of May-June between



Fig. 1 — Schematic diagram of solar photoreactor

9 a.m and 5 p.m. The degradation of pollutants from the effluents with the pilot plant solar reactor was monitored using COD values. Solar light intensity was measured for every 30 min using LT Lutron LX-10/A Digital Lux meter and the intensity was $1250 \times 100 \pm 100$ lux. The intensity was nearly constant during the experiments.

Results and Discussion

Heterogeneous photocatalysis plays a major role in detoxifying hazardous pollutants to innocuous end products. The rate and extent of photocatalytic degradation process are affected by variables such as pH, percentage of Fevicol content, initial concentration, catalyst loading, etc. The effects of these variables were studied using both F-T coating and suspended TiO_2 in falling film photoreactor. The characteristics values of effluent discharged from the gelatin industry are shown in Table 1. In all the experiments 10 L of the gelatin industry wastewater was used with an initial COD of 2100 ppm (diluted 5 times) and pH of 5.5.

The falling film flow reactor (Fig. 1) was employed to test the photocatalytic activity of F-T thin film and suspended TiO_2 . Preliminary studies showed very poor COD removal (2%) with solar irradiation without catalyst for nearly 4h and 7% COD reduction by adsorption on suspended TiO_2 alone without solar irradiation. The mineralization efficiency at 4 h treatment using 10 wt% F-T coating was 40.5 % for the effluent (Fig. 2b) whereas 76.5% of degradation was observed with suspended TiO_2 (Fig. 2a). The results indicate that gelatin effluent can be effectively degraded on irradiation with solar light in presence of TiO_2 . This degradation is caused mainly by hydroxyl radical, a strong oxidizing species produced by TiO_2 on irradiation with solar light (Eqns.1–5)^{1,6}.

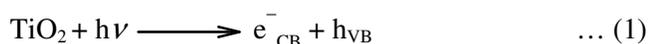


Table 1 — Composite raw effluent analysis report

S. NO	Parameters	Average
1	pH	8.04
2	TSS ppm	8966
3	TDS ppm	11013
4	COD ppm	11733
5	BOD ppm	5700



Effect of semiconductors

The semiconductors, TiO_2 anatase (band gap energy, Eg 3.2 eV), Homemade TiO_2 (band gap energy, Eg 3.2 eV), Fe_2O_3 (Eg 2.2 eV, ZnO (nano), ZnO (commercial) (Eg 3.2 eV), and TiO_2 -P25 (band gap energy, Eg 3.2 eV) were used for the preparation of fevicol film coating and the degradation of gelatin industry effluent was analyzed with these catalysts. The results are shown in Table 2. All these catalysts coated on acrylic plastic sheet, effectively degraded gelatin industry effluent under sun light (Table 2).

The results reveal that immobilized homemade TiO_2 is more efficient in the treatment of gelatin industry effluent when compared to immobilized TiO_2 (anatase), TiO_2 -P25, Fe_2O_3 , ZnO (nano), ZnO

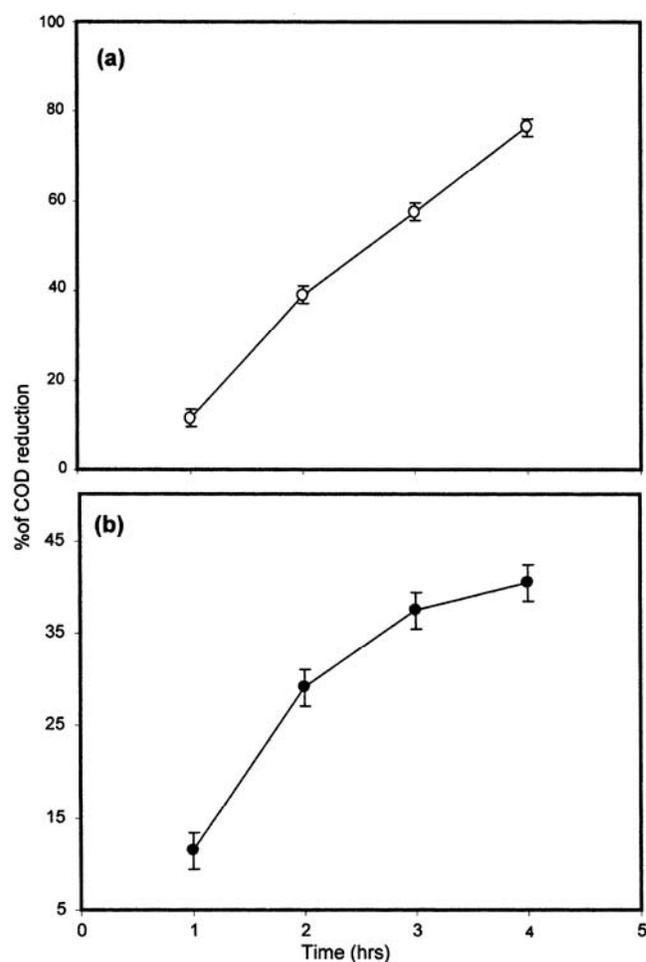


Fig. 2 — Preliminary degradation of effluent (a) suspended TiO_2 and (b) F-T thin film, Effluent concentration = 2100 ppm, catalyst suspended = 1 g L^{-1} ; $10 \text{ g}/0.43 \text{ m}^2$, pH = 5.0, airflow rate = 8.1 mL s^{-1} , irradiation time = 4 h. $I_{\text{Solar}} = 1250 \times 100 \pm 100$ lux

Table 2 — Effect of various photocatalysts with 10% fevicol on photodegradation^a using falling film photoreactor

Semiconductor	% of COD (removal)
TiO ₂ (anatase)	10.5
Home prepared TiO ₂	57.0
ZnO (commercial)	26.0
Fe ₂ O ₃	37.5
ZnO (nano)	25.0
CdS	21.8
TiO ₂ -P25	12.0

^aEffluent concentration = 2100ppm, catalyst coated = 10g/0.43m², pH = 5.5, airflow rate = 8.1 mL s⁻¹, irradiation time = 4h. I_{solar} = 1250×100±100Lux.,

(commercial) and CdS. Although the catalysts could be immobilized on aluminum and polymer strips using ‘Fevicol’, they get easily peeled off after illumination. Also, use of organic solvents along with adhesives for immobilization of the catalysts did not yield positive results. These catalysts in suspended form showed the same trend for gelatin industry effluent treatment. Therefore, the treatment of gelatin industry effluent was further studied in detail using homemade titania.

Effect of different % of Fevicol

Slurries comprising Fevicol and TiO₂ in suitable weight proportions (5, 10, 15 and 20 wt% Fevicol) were prepared and coated on acrylic plastic sheet. The relation between amount of Fevicol immobilized in the catalyst and percentage of COD reduction is shown in Fig. 3. It is observed that the degradation increases with the increase in the amount of Fevicol up to 10 wt%, and then decreases. The decrease at high Fevicol concentrations may be due to the enhancement of light reflectance by the Fevicol and decrease in the percentage of TiO₂.

Effect of solution pH

The effect of pH on the photocatalytic degradation of effluent was tested in the pH range of 3 to 9 and results are presented in Fig. 4. After 3 h of irradiation, the COD reduction values are 50.5, 51.5, 48.8 and 42.8% for TiO₂ suspension (Fig. 4a) and 23.1, 36.7, 11.2 and 9.5% for F-T thin film (Fig. 4b) at pH 3, 5, 7 and 9, respectively. In both processes higher efficiency is observed at pH of 5. The order of efficiency is found to be pH 5 > pH 3 > pH 7 > pH 9. The Zero point charge of TiO₂ is at pH 6.8. Hence, the increased degradation in acidic pH is due to enhanced adsorption of negatively charged effluent on the

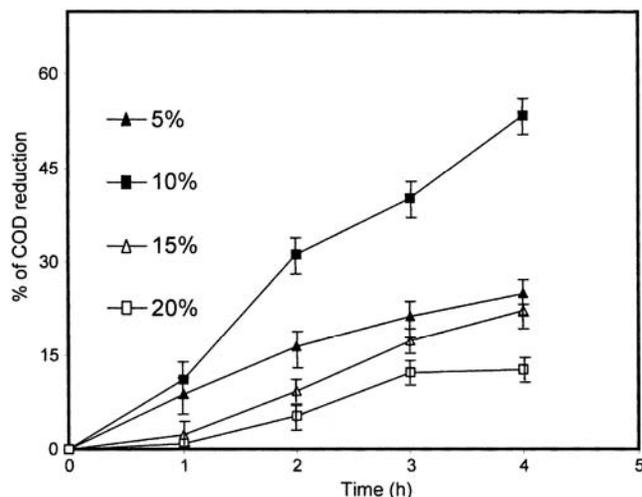


Fig. 3 — Effect of various percentage content of fevicol at TiO₂ Effluent concentration = 2100 ppm, catalyst coated = 10g/0.43 m², pH = 5.0, airflow rate = 8.1 mL s⁻¹, irradiation time = 4 h, I_{solar} = 1250×100±100 lux

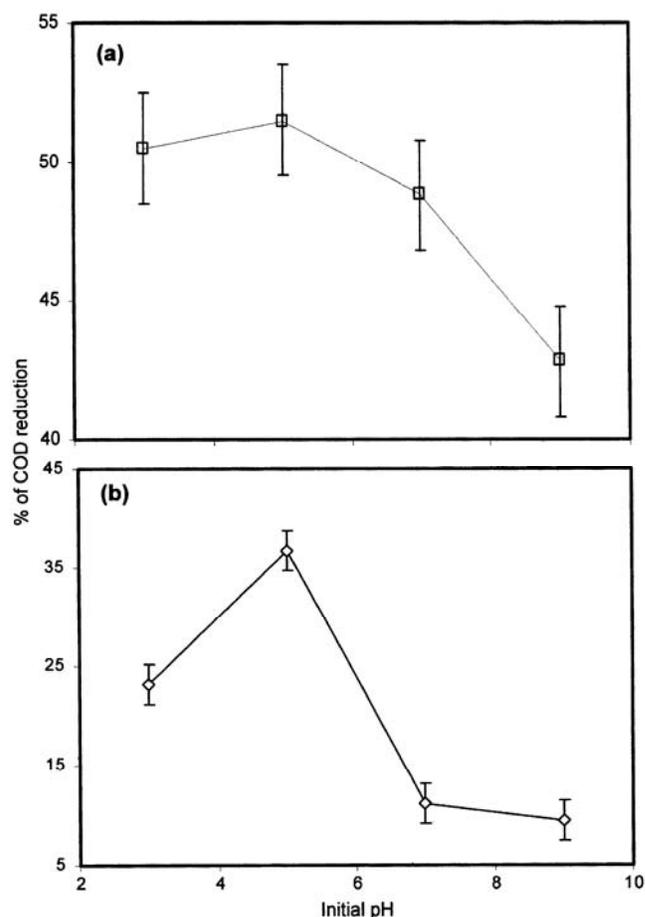


Fig. 4 — Effect of solution pH: (a) suspended TiO₂ and (b) F-T thin film, Effluent concentration = 2100 ppm, catalyst suspended = 1 g L⁻¹; 10g/0.43 m², airflow rate = 8.1 mL s⁻¹, irradiation time = 3 h, I_{solar} = 1250×100±100 lux

surface of TiO_2 that carries positive charge at acidic pH . Since the protons are potential determining ions, the surface charge of TiO_2 is influenced by pH of the solution¹⁸.

Effect of photocatalyst dosage

The influence of the photocatalyst dosage on the degradation of gelatin industry effluent has been investigated employing different concentrations of suspended TiO_2 and F-T thin film (Fig. 5). The percentage of COD reduction values increase from 27.1 to 57.5% with the increase of suspended TiO_2 concentration (Fig. 5a) from 5 to 10.0 g (0.5 g L^{-1} to 1.0 g L^{-1}). Further increase from 10 to 12.5 g (1.25 g L^{-1}), decreases COD reduction from 57.5 to 48.5%. In the case of F-T thin film (Fig. 5b) increase of catalyst loading from $5\text{g}/0.43 \text{ m}^2$ to $10\text{g}/0.43 \text{ m}^2$ increase the percentage of COD reduction from 9.9 to 36.1%. Further increase of catalyst concentration from $10\text{g}/0.43 \text{ m}^2$ to $12.5\text{g}/0.43 \text{ m}^2$ decreases the removal rate. Enhancement of removal rate is due to (i) the increase in the number of effluent molecules adsorbed on the catalyst, (ii) the increase in the density of catalyst particles in the area of illumination. Hence under these experimental conditions 10g (1g L^{-1}) of suspended TiO_2 and $10\text{g}/0.43 \text{ m}^2$ were found to be optimum for efficient treatment of effluent under both processes. The decrease in efficiency at higher concentrations is probably due to light reflectance of catalyst particles and screening effect resulting from the opacity of the solution⁷.

Effect of effluent concentration

The effect of effluent concentration on the COD reduction for of TiO_2 suspended and F-T thin film processes was performed to find out the optimum effluent concentration for maximum efficiency. For the effluent concentrations 525, 1250, 1750 and 2100 ppm (diluted with respect to water) the percentages of COD reduction in the suspended TiO_2 process are 100, 98.4, 93.5 and 52.7% respectively. In F-T thin film process the percentages of COD reductions for the same effluent concentrations are 90.0, 60.5, 37.9 and 26.0%, respectively. In both processes increase in effluent concentration decreases the percentage of COD reduction (conditions- $\text{pH} = 5$, airflow rate = 8.1 mL s^{-1} , catalyst suspended = 1 g L^{-1} ; $10\text{g}/0.43 \text{ m}^2$, irradiation time = 3h, $I_{\text{solar}} = 1250 \times 100 \pm 100 \text{ lux}$). The rate of degradation relates to the probability of $\cdot\text{OH}$ radical formation on catalyst surface and probability of $\cdot\text{OH}$ radical reacting with effluent. For all initial

pollutant concentrations, the catalyst, oxidant and light intensity are same. Since the generation of hydroxyl radical remains constant, the probability of effluent to react with hydroxyl radical decreases at high initial concentrations.

Reusability

The reusability of F-T thin film has been studied and compared with suspended TiO_2 in falling film photoreactor. Degradation study was carried out for five runs under identical reaction conditions. After complete degradation, the suspended catalyst was separated and washed with large amount of deionized

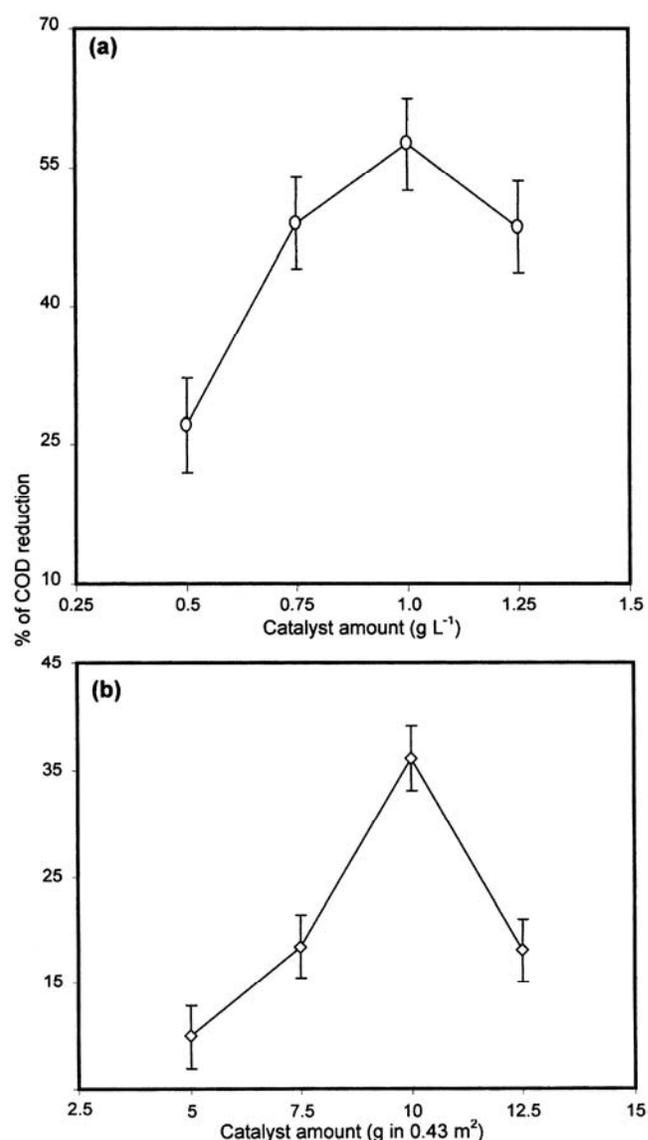


Fig. 5 — Effect of catalyst concentration: (a) suspended TiO_2 and (b) F-T thin film, Effluent concentration = 2100 ppm, $\text{pH} = 5$, airflow rate = 8.1 mL s^{-1} , irradiation time = 3 h, $I_{\text{solar}} = 1250 \times 100 \pm 100 \text{ lux}$

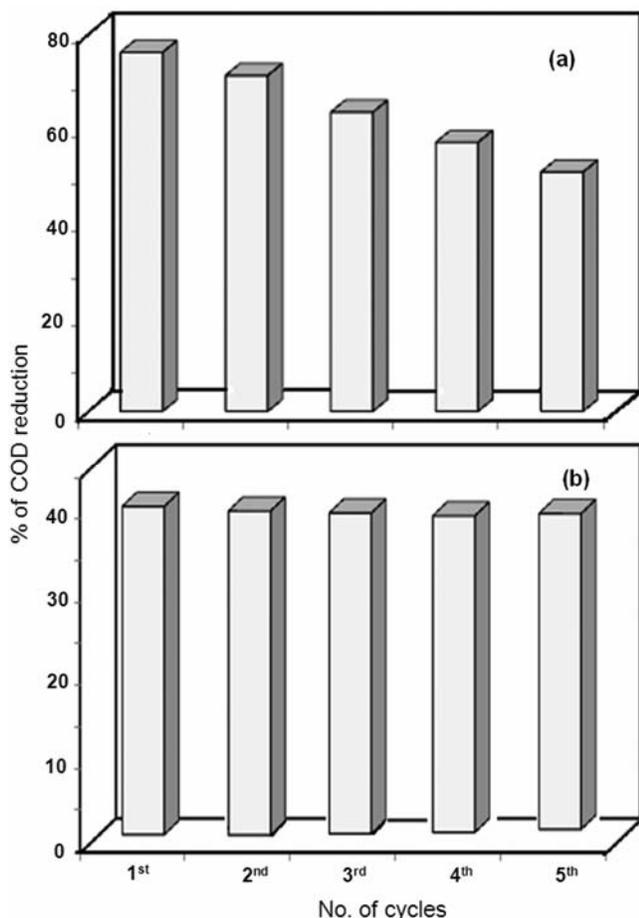


Fig. 6 — Reusability of the catalyst on the degradation of gelatin effluent for three runs: (a) suspended TiO₂ and (b) F-T thin film, Effluent concentration = 2100 ppm, catalyst suspended = 1 g L⁻¹; 10g/0.43 m², pH 5, airflow rate = 8.1 mL s⁻¹, irradiation time = 4 h, I_{solar} = 1250×100±100 lux

water. The washed catalyst was dried in atmospheric conditions and in hot air oven at 100°C for 30 min and used for second run. Figures 6a and b show gelatin effluent degradation results of home prepared TiO₂ suspended and F-T thin film respectively for five runs. F-T thin film exhibits remarkable photostability as the degradation percentages are 39.4, 38.9, 38.5, 38.0 and 37.8 in first, second, third, fourth and fifth runs respectively for 4 h. It was found that even after four cycles using the same batch of F-T thin film, the photocatalytic activity of the coated TiO₂ was not affected significantly when compared to fresh catalyst. But in case of suspended TiO₂ 76.0, 71.1, 63.3, 56.9 and 50.6% degradations were observed in first, second, third, fourth and fifth runs respectively for 4 h. In suspended TiO₂ process the decrease in efficiency is significant. Furthermore separation of catalyst from

suspended TiO₂ is difficult whereas thin film can be used after wash. This reveals that F-T film is stable and can be reused for several cycles. Hence F-T process is applicable for continuous treatment of effluent.

Conclusion

Homemade TiO₂ is found to be more efficient in the treatment of gelatin industry effluent than other semiconductor photocatalysts. Optimum pH and catalyst loading on the pilot scale solar reactor are 5 and 10g/0.43m², respectively. Though the treatment by suspended TiO₂ is more efficient than thin film TiO₂ in the first cycle, thin film TiO₂ is more stable, reusable for several cycles without significant loss of activity. Hence, the solar treatment of gelatin industry effluent with F-T catalyst using falling flow reactor is cost effective and can be used for the continuous treatment of any industrial effluent.

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