

Article

Preparation and Characterization of the TiO₂ Immobilized Polymeric Photocatalyst for Degradation of Aspirin under UV and Solar Light

Debjani Mukherjee, Shahzad Barghi and Ajay K. Ray *

Department of Chemical and Biochemical Engineering, Western University, London, ON N6A5B9, Canada; E-Mails: dmukher4@alumni.uwo.ca or dr.debjani9@gmail.com (D.M.); sbarghi2@uwo.ca (S.B.)

* Author to whom correspondence should be addressed; E-Mail: aray@eng.uwo.ca; Tel.: +1-519-661-2111 (ext. 81279); Fax: +1-519-661-3498.

Received: 1 September 2013; in revised form: 2 December 2013 / Accepted: 6 December 2013 / Published: 27 December 2013

Abstract: The traditional use of TiO₂ powder as a photocatalyst for degradation of organic compounds has several post-degradation treatment problems, such as filtration, precipitation, *etc.* A novel method was developed to immobilize TiO₂ to minimize/eliminate such problems. Polymeric membrane was used as a base material, over which the TiO₂ photocatalyst was immobilized as a thin layer. Preparation and characterization of five different types of polymeric/TiO₂ film photocatalysts were elucidated. The catalysts' films were cross-linked by physical, chemical, and combination of these two processes. The polymers used in the formulation of the catalysts membranes are nontoxic in nature (approved by the World Health Organization (WHO) and Food and Drug Administration (FDA)). The morphology of the films were studied by SEM. Photocatalytic degradation of acetylsalicylic acid was carried out to study the efficacy and efficiency of the polymeric membrane based TiO₂ as photocatalysts under both UV and solar light irradiation. The degradation was observed to be dependent on the catalyst loading as well as the film thickness. The effects of the types of cross-link bonds on the photocatalytic degradation were also investigated.

Keywords: TiO₂; photocatalysis; water treatment; polymeric membrane; immobilized photocatalyst

Nomenclature

C and C ₀	Concentration, ppm
K	Langmuir-Hinshelwood rate constant
K	Langmuir constant
PVA	Polyvinyl alcohol
PVP	Polyvinyl pyrrolidone
P25 TiO ₂	Degussa P25 Titanium dioxide
SEM	Scanning Electron Microscopy
CL	Cross link

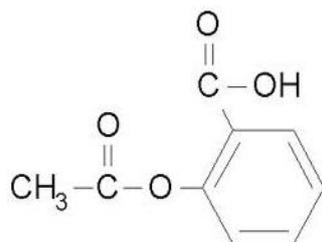
Subscripts

Sl	slurry
f-d	Freeze dried
Ald	Aldehyde
UV	Ultraviolet
H	Heat treated
f-d/UV	Freeze dried UV treated

1. Introduction

One of the most pressing environmental issues of present and future is the effective protection and utilization of the precious fresh water resources of the world. According to the World Health Organization (WHO) more than one billion people in the world are suffering from the lack of access to clean potable water. Waterborne infections account for 80 percent of all infectious diseases in the world. Pharmaceuticals, in general, enter the environment through different pathways, resulting in the contamination of ground/underground water, where bacteria are most likely the primarily affected organisms. Due to high intake of non-steroidal anti-inflammatory drugs (NSAIDs), their presence in drinking water has been widely reported [1]. Aspirin belongs to this class of medications called NSAIDs. NSAIDs are the most frequently prescribed agents to treat fever, pain, arthritis, *etc.* In addition to its effects on pain, fever, and inflammation, aspirin also has an important inhibitory effect on platelets in blood. This antiplatelet effect is used to prevent blood clot formation inside arteries, particularly in individuals who have atherosclerosis (narrowing of the blood vessels), or are otherwise prone to develop blood clots in their arteries preventing heart attack and strokes. Molecular structure of aspirin is shown in Figure 1.

In aqueous solutions, organic compounds can undergo photochemical transformations with sunlight via direct or indirect photoreactions [2]. Such photochemical degradation can be one of the major transformation processes and one of the factors that control the ultimate fate of organic pollutants in the environment. Various technologies are in use to purify aqueous municipal and industrial effluents containing pharmaceutical substances, before entering surface waters. Among them, advanced oxidation processes (AOPs) have been of major interest in recent years.

Figure 1. Molecular structure of aspirin.

Among all the Advance Oxidation Processes (AOPs), Titanium Dioxide (TiO_2) photocatalytic oxidation holds a great deal of promise to address this issue due to the low cost of TiO_2 and its chemical stability. It is also remarkably active, and non-toxic over a wide range of pHs. In general, the goal of photocatalysis in water treatment is transformation, deactivation, and, finally, mineralization of environmentally persistent compounds. The TiO_2 photocatalyst is able to utilize sunlight and air to produce many reactive species, including the powerful and non-selective oxidant hydroxyl radicals, to destroy organic compounds. One of the major drawbacks is expensive filtration technique needed to remove the slurry TiO_2 from the purified water [3,4]. This problem has resulted in development of several kinds of immobilization techniques to immobilize the TiO_2 powder, which may reduce the post degradation expenses and time. TiO_2 in anatase, Degussa form has been immobilized by several methods. The design and development of an immobilized thin catalyst film facilitates commercial-scale applications of TiO_2 -based photocatalytic processes for water treatment significantly. The dimensionality associated with the structure of a TiO_2 material can affect its properties and functions, including its photocatalytic performance, and also, more specifically, its surface area, adsorption, reflectance, adhesion, and carrier transportation properties [5]. Immobilization of TiO_2 photocatalyst eliminates the need for the separation of the catalyst particles from the treated liquid and enables the contaminated water to be treated continuously. The catalyst film is porous and can therefore provide a large surface area for the degradation of contaminant molecules. If a conductive material is used as the support, the catalyst film can be connected to an external potential source to remove excited electrons to reduce electron-hole recombination, thereby, significantly improving the process efficiency [6–9]. Di Paola *et al.* [10] reviewed different type of TiO_2 catalysts and claimed that although many of these photocatalysts were effective for the photodecomposition of many pollutants, most of them do not allow a complete mineralization of the starting compounds.

Several researches have been carried out on immobilization of the TiO_2 [11,12]. Two obvious problems arising from this arrangement: the accessibility of the catalytic surface to the photons and the reactants and a significant influence of the external mass transfer resistance particularly at low fluid flow rate, due to the increasing diffusion length of the reactant from the solution to the catalyst surface [13]. Maedaa [14] presented a comprehensive review of different reactor designs for air- or water-purification with the main emphasis on the enlargement of reactive surface area and improvement of mass transfer. Several kinds of film photocatalysts have been formulated by researchers, such as TiO_2 loaded carbon fiber [15], silicone- TiO_2 polymeric composite [16], Polypropylene/clay with TiO_2 composite [17], and TiO_2 -PVP (Polyvinyl pyrrolidone) nano-composite [18]. Ochiai and Fujishima [19] fabricated a novel photocatalytic filter, titanium-mesh sheet modified with TiO_2 . The titanium mesh sheet was claimed to be highly flexible with a large

contact area with a minimum pressure drop. Modification of the photocatalyst with a suitable cocatalyst was carried out to provide an active redox site for water splitting [20]. Due to challenges associated with the use of UV light, several attempts have been made to use visible light instead. Pelaeza *et al.* [21] presented different strategies for the modification of TiO₂ photocatalyst for the utilization of visible light along with comprehensive studies on the photocatalytic degradation of contaminants.

These immobilization techniques have been reported to reduce the cost of filtration and also in some cases increase the efficiency of TiO₂ as photocatalyst, due to the synergistic effect of the substrate and TiO₂. All these techniques have been proved to be successful though being expensive and time consuming their use has been limited. In this study, a polymeric film was prepared as a substrate for immobilization. The degradation of aspirin was carried out to measure and compare the photocatalytic efficiency of the films. Mass transfer limitations become a dominant factor when immobilized photocatalyst film is used, which usually lead to a lower overall degradation rate compared to the suspended catalyst systems [22,23].

The degradation kinetics of aspirin follows the Langmuir-Hinshelwood (L-H) model.

$$r = -\frac{dC}{dt} = \frac{kKC}{1 + KC} \quad (1)$$

where r is the photocatalytic degradation rate, k is the L-H kinetic rate constant, and K is the Langmuir adsorption constant. A linear plot of $1/r$ against $1/C$ is often used to estimate the L-H rate constants, k , and the Langmuir adsorption constant, K , for aspirin in the photocatalytic degradation reaction. The analysis is based on the occurrence of the reactions on the active site of the catalysts where hydroxyl radicals are actually formed.

$$\frac{1}{r} = \frac{1}{kK} \frac{1}{C} + \frac{1}{k} \quad (2)$$

2. Experimental Section

2.1. TiO₂ Immobilization Procedure

2.1.1. Preparation of Polymeric/TiO₂ Membranes

9% *w/v* of PVA and 4% *w/v* Gelatin were dissolved and mixed properly in distilled water to get a transparent solution. Next, 8% *w/v* of PVP was dissolved in a solution of ethyl alcohol and water (in 2:1 ratio) and added to the PVA-Gelatin solution and the reaction was carried out at room temperature. The solution was stirred for 15 min, followed by dispersion of 16% *w/w* TiO₂ Degussa P25 powder in the mixture. Thereafter, the polymeric/TiO₂ solutions were cross-linked by physical, chemical, and physico-chemical methods. The polymer matrix used for immobilization may be degraded under ultraviolet light however in the context of this research and during all the experiments such a phenomenon was observed. Apparently the degradation rate of polymer matrix is much longer than the duration of the experiments.

2.1.2. Physical Cross-Linking Methods

2.1.2.1. Freeze Drying

The TiO₂ dispersed polymeric solution was then physically cross-linked by storing the solution below zero degrees centigrade. The polymeric solutions were stored at different temperatures ranging from 0 to −10 °C for different time intervals of 1, 3, 5, 7, 10, 15, 24 (h). It was found that the samples stored for 5 h showed the best results under solar and UV lights. Solutions stored for less than 5 h showed very soft and flexible films, which were partially dissolved in water during the photo-degradation reaction, while the ones stored for longer than 5 h formed mechanically strong catalysts due to more cross linking, but showed lower degradation. The lower degradation rate was most probably due to blockage of the TiO₂ active site by the cross-linked polymers. Therefore, the freeze-dried film was cross-linked physically at −2 °C for 5 h (optimum condition).

2.1.2.2. Heat Treatment

Cross-linking also occurs at higher temperatures. Generally, cross-linking increases with increasing temperature, therefore the prepared polymeric/TiO₂ solution was placed in an oven for different times, at different temperatures, to cross-link. Due to deactivation of PVP at 120 °C and due to uneven distribution of temperature in the oven, it was found that 105 °C was the optimum temperature for cross-linking. Samples were kept at 105 °C for different period of times between 5 and 120 min. The solution, which had been kept for 10 min, showed the best results with respect to the desired mechanical properties and degradation efficiency.

2.1.3. Chemical Cross-Linking Methods

2.1.3.1. Acetaldehyde Treatment

Aldehydes are known to initiate cross-linking of PVP polymer solution instantly. Acetaldehyde chemically cross-links with PVP in the polymeric solution and instantly forms a membrane. After several experiments, it was found that 0.5 mL of 2% acetaldehyde at room temperature was sufficient to crosslink the polymer solution completely. The membrane was then dipped in distilled water and washed 3 times to remove the unreacted acetaldehyde traces.

2.1.3.2. UV Treatment

Polymeric solutions with dispersed TiO₂ were exposed to UV light of 275 nm wavelength for different periods of time (2, 5, 7, 10, 20, 30, and 60 min). It was observed that exposure for 10 min provided the best results among all the samples. Samples exposed for 2–7 min did not form mechanically strong films, which in turn degraded in the aqueous solution during the photo-degradation process. The catalyst films formed by exposure of 20–60 min was mechanically strong but, due to high cross-linking effects, the TiO₂ particles got entangled within polymer matrix, resulting in blockage of the active sites and lower degradation efficiency.

2.1.3.3. Freeze-Dried and UV Treated

The polymeric solution was prepared following the aforementioned freeze drying method (kept at 0 °C for 5 h) and then exposed to UV lamp of 275 nm wavelength for 10 min to cure the polymeric membrane.

3. Characterization and Degradation of Aspirin

Optical microscopy, Scanning Electron Microscopy (SEM, Hitachi F-4000) and Fourier transform Infra Red were employed to characterize the immobilized TiO₂ photocatalyst film. SEM studies of the film photocatalysts revealed the specific pore volume and pore density. The measuring scale was 2.5 μm. Catalyst films were also subjected to Fourier Transform Infra Red (FTIR) Spectroscopy. The specimens were prepared as thin and homogenous films. FTIR spectra were measured in the wave number range 400–4000 cm⁻¹.

The photodegradation reactions were carried out in batch reactors, in presence of both solar and UV lights with five different kinds of polymeric/TiO₂ catalyst films. The batch reactors were 250 mL in volume, containing aspirin solutions under a UV lamp of 22 mW/cm² intensity and the solar stimulator of light intensity 27 mW/cm². The concentrations of the degraded aspirin solutions were analyzed using a UV-Vis Agilent spectrophotometer at 270 nm.

4. Results and Discussions

4.1. Optical Microscopy

The polymeric/TiO₂ catalyst films were subjected to optical microscopy (OM) to observe their porous structures. The freeze-dried film showed a spongy porous structure. The heat-treated films were observed to have a highly porous 3D structure, which made the films remain buoyant in water. The acetaldehyde and UV treated films showed solid matrices with very few pores. The UV-Freeze-dried treated films showed a spongy structure similar to freeze-dried but with fewer number of pores. Figures 2–6 show the structures of the five different immobilized photo-catalyst films.

Figure 2. Optical Microscope image of freeze-dried film.

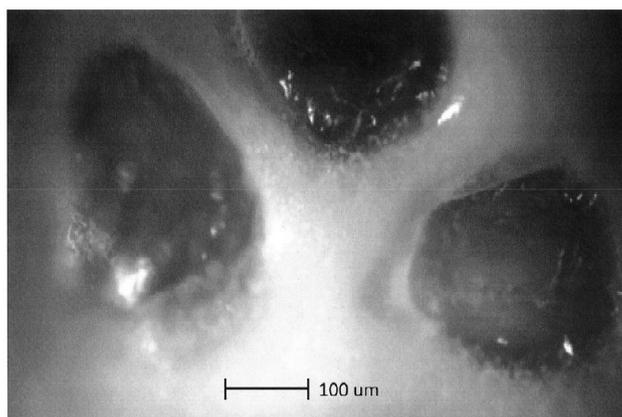


Figure 3. Optical Microscope image of heat-treated film.

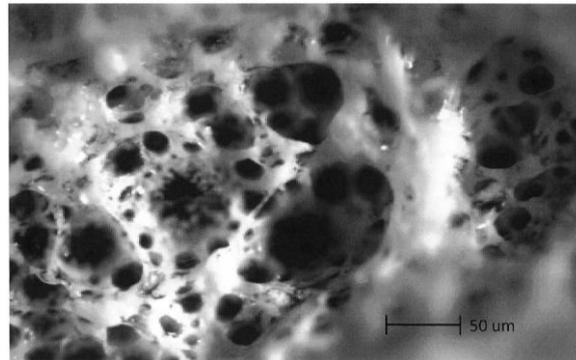


Figure 4. Optical Microscope image of UV-treated film.

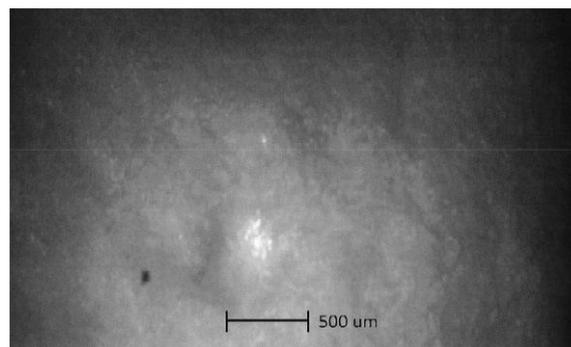


Figure 5. Optical Microscope image of UV-treated and freeze dried film.

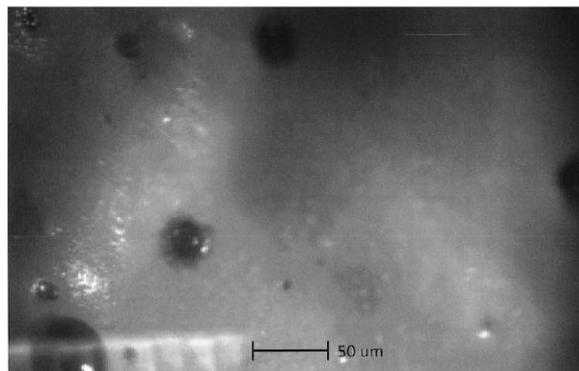
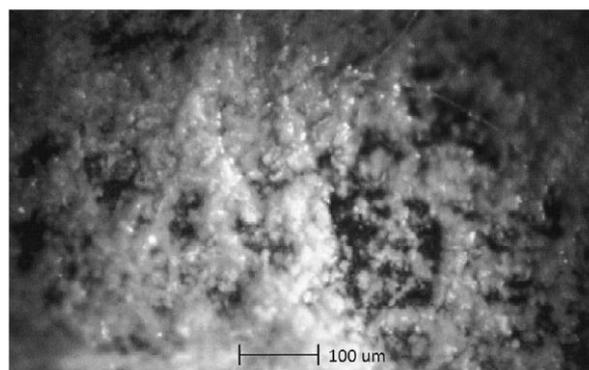


Figure 6. Optical Microscope image of acetaldehyde-treated film.



4.2. Scanning Electron Microscopy (SEM) Study

The polymeric/TiO₂ catalyst film thickness ranged from 0.45 mm to 2 mm. The micrographs taken by scanning electron microscopy revealed a three-dimensional network structure, which was typical for a porous material. Figure 7 shows the porous structure of the freeze-dried catalyst film. Obviously, the freeze-dried membrane is rather homogeneous, interspersed with pores of various diameters, ranging from 50 to 300 μm. The average pore area was found to be 572 μm². The pore density ranged from 7 to 10 pores per mm² for the freeze-drying film. The pore density was 12–15 pores per mm² for the heat-treated polymeric/TiO₂ catalyst film. The acetaldehyde and UV treated samples showed almost no pores and the freeze-dried-UV treated film showed 3–5 pores per mm². Figures 7–11 show the SEM images of the samples.

Figure 7. SEM image of freeze-dried polymeric/TiO₂ catalyst membrane.

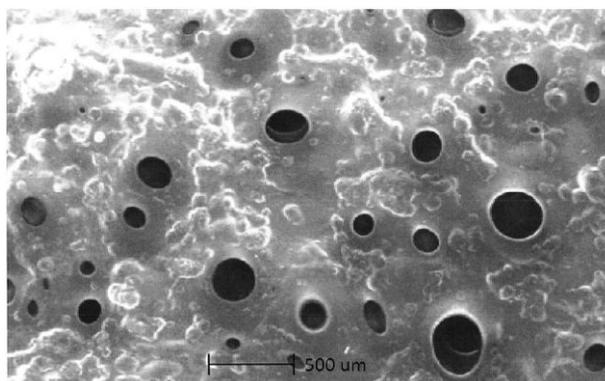


Figure 8. SEM image of heat-treated membrane.

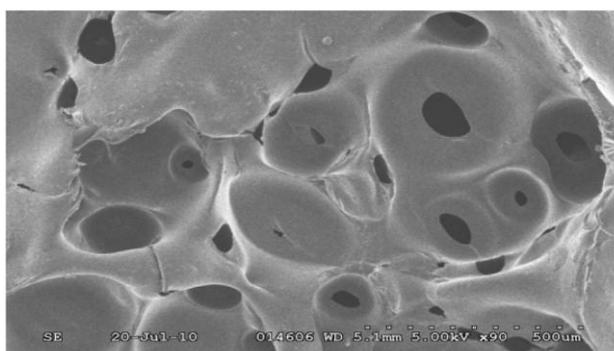


Figure 9. SEM image of UV-treated membrane.

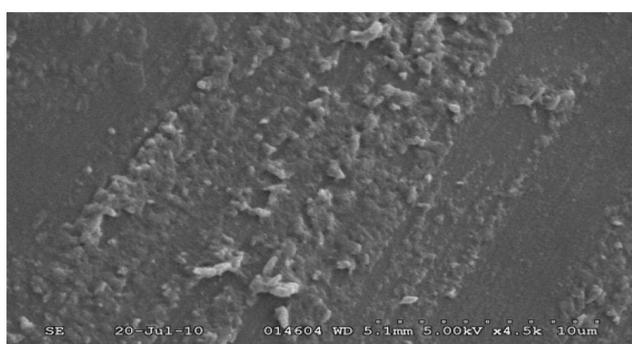


Figure 10. SEM image of UV treated and freeze-dried membrane.

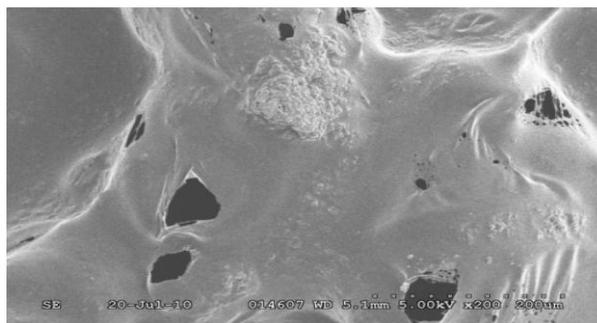
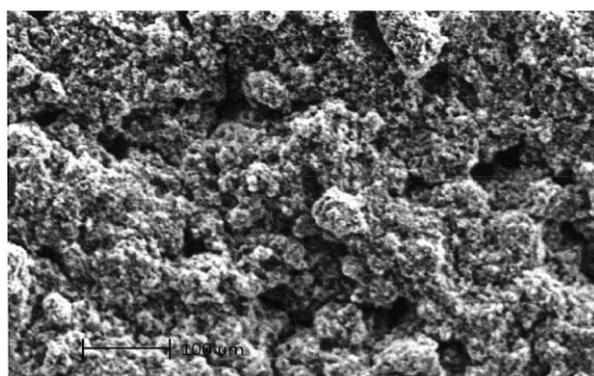


Figure 11. SEM image of acetaldehyde-treated composite membrane.



4.3. Degradation of Acetylsalicylic Acid (Aspirin)

Cross-linking affected degradation of aspirin under UV and solar light over different photocatalyst films. As shown in Figures 11–13, the freeze-dried catalyst was more efficient in degrading aspirin compared to the other photocatalyst films in presence of solar light. Although, the freeze-dried catalyst showed higher degrading efficiency under UV light, the efficiency decreased rapidly with time. UV radiation activates cross-linking and, with more cross-linking, less TiO_2 active site would be available, resulting in gradual decrease of the degradation rate with time. The freeze-dried catalysts were useable for a short period of time as some polymeric flakes leached out into the aqueous system after six to seven hours of use. Although these polymers are nontoxic and have been approved by the FDA and WHO, and can be removed by a simple filtration method, such a phenomenon may restrict their application and more investigation is required to improve their mechanical stability. On the other hand, the heat-treated photocatalyst film was buoyant and could be used several times for the degradation of organic model compound. The UV treated and UV-freeze-dried catalysts showed the slowest degradation rate. The aldehyde treated catalyst was found to remain in submerged condition in water during the reaction and also showed a slower degradation rate. The UV treated catalyst membrane showed morphological characteristics, the same as UV-freeze-dried catalyst, and both catalysts were observed to follow almost the same rate of degradation in presence of solar light and UV light. The UV treated catalyst showed higher tensile strength due to formation of strong cross-linking bonds but became blue after the UV treatment. This blue colorization is due to the entrapped electrons, which delay the degradation rate. Table 1 shows the reaction rate constant, k , for different TiO_2 immobilized catalysts under UV and solar radiation.

Figure 12. Effect of different cross-linked TiO₂ films on the degradation of aspirin under UV light ($C_0 = 2$ ppm, $I = 22$ mW/cm², pH = 4.5).

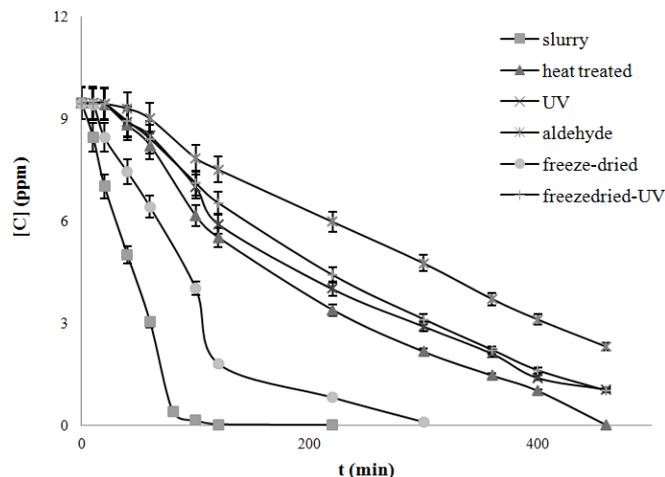
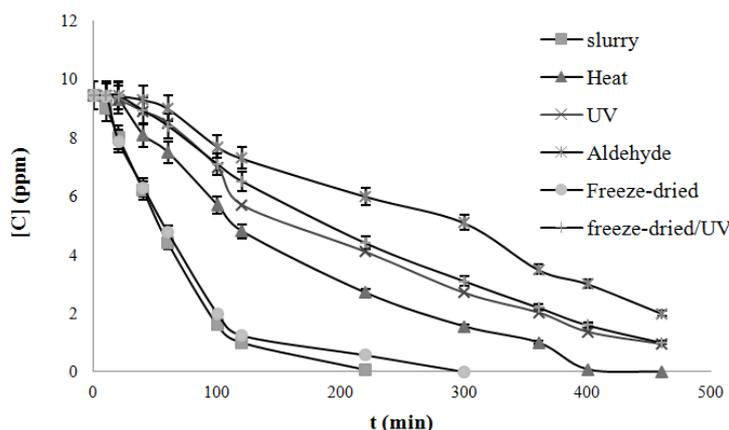


Table 1. Comparison between reaction rate constants for different catalysts.

Catalysts	Freeze dried	Heat treated	UV treated	Acetaldehyde treated	Freeze-dried UV treated
k, mg/L/min UV light	0.050	0.019	0.017	0.015	0.024
k, mg/L/min Solar light	0.079	0.022	0.019	0.017	0.027

Figure 13. Effect of cross-linkages on degradation of aspirin under solar light ($C_0 = 2$ ppm, $I = 27$ mW/cm², pH = 4.5).



5. Conclusions

A cross-linked polymeric membrane was used to immobilize TiO₂ photocatalyst to avoid costly post-treatment processes, such as filtration. Five different immobilized photocatalysts were prepared, namely heat-treated, aldehyde-treated, UV-treated, freeze-dried and UV-freeze-dried. It was observed that the freeze-dried catalyst film had a porous structure and the highest degradation efficiency. The spongy 3D structure of the catalyst also made it capable of adsorbing larger amounts of organic/inorganic pollutants on its active sites, which in turn increased the degradation rate of Aspirin. The freeze-dried film was not mechanically strong, and failed to keep its identity after six to seven

hours. The UV-treated catalyst films showed very few or almost no pores, while the heat-treated photocatalyst film contained several air pockets, which made it buoyant in aqueous solutions. The buoyant nature of the heat-treated film may be exploited to keep the catalyst film afloat and exposed to solar light for the continuous degradation of pollutant in water. The toxic nature of aldehyde reduces the chance of using aldehyde-treated catalyst films for drinking water purification. The UV-treated catalysts showed higher tensile strength, however, due to strong cross-linkage effect of UV light, these films have fewer active sites of TiO₂ available for interacting with the photons.

Conflicts of Interest

The authors declare no conflict of interest.

References

1. Liu, C.-C.; Hsieh, Y.-H.; Lai, P.-F.; Li, C.-H.; Kao, C.-L. Photodegradation treatment of azo dye waste water by UV/TiO₂ process. *Dye. Pigment.* **2006**, *68*, 191–195.
2. Fujishima, A.; Honda, K. Electrochemical photolysis of water at a semiconductor electrode. *Nature* **1972**, *238*, 37–38.
3. *Photocatalytic Purification and Treatment of Water and Air*; Al-Ekabi, H.A., Ollis, D., Eds.; Elsevier: Amsterdam, The Netherlands, 1993.
4. Andronic, L.; Duta, A. The influence of TiO₂ powder and film on methyl orange degradation. *Mater. Chem. Phys.* **2008**, *112*, 1078–1082.
5. Vincenzo, A.; Marianna, B.; Vittorio, L.; Giovanni, P.; Leonardo, P.; Sedat, Y. Overview on oxidation mechanisms of organic compounds by TiO₂ in heterogeneous photocatalysis. *J. Photochem. Photobiol. C* **2012**, *13*, 224–245.
6. Daneshvar, N.; Salari, D.; Khataee, A.R. Photocatalytic degradation of azo dye acid red 14 in water: Investigation of the effect of operational parameters. *J. Photochem. Photobiol. A* **2003**, *157*, 111–116.
7. Akira Fujishima, A.; Rao, T.N.; Tryk, D.A. Titanium dioxide photocatalysis. *J. Photochem. Photobiol. C* **2000**, *1*, 1–21.
8. Chen, D.; Ray, A.K. Photocatalytic kinetics of phenol and its derivatives over UV irradiated TiO₂. *Appl. Catal. B* **1999**, *23*, 143–157.
9. Rizzo, L.; Koch, J.; Belgiorno, V.; Anderson, M.A. Removal of methylene blue in a photocatalytic reactor using polymethylmethacrylate supported TiO₂ nanofilm. *Desalination* **2007**, *211*, 1–9.
10. Di Paola, A.; Garc á-López, E.; Marc à, G.; Palmisano, L. A survey of photocatalytic materials for environmental remediation. *J. Hazard. Mater.* **2012**, *211–212*, 3–29.
11. Dung, N.T.; van Khoa, N.; Herrmann, J.-M. Photocatalytic degradation of reactive dye RED-3BA in aqueous TiO₂ suspension under UV-visible light. *Int. J. Photoenergy* **2005**, *25*, 250–255.
12. Kalfa, O.M.; Alçinkaya, Ö.; Türker, A.R. Synthesis of nano B₂O₃/TiO₂ composite material as a new solid phase extractor and its application to preconcentration and separation of cadmium. *J. Hazard. Mater.* **2009**, *166*, 455–461.

13. Rashed, M.N.; El-Amin, A.A. Photocatalytic degradation of methyl orange in aqueous TiO₂ under different solar irradiation sources. *Int. J. Phys. Sci.* **2007**, *2*, 73–81.
14. Maedaa, K. Photocatalytic water splitting using semiconductor particles: History and recent developments. *J. Photochem. Photobiol. C* **2011**, *12*, 237–268.
15. Shi, J.; Zheng, J.; Wu, P.; Ji, X. Immobilization of TiO₂ films on activated carbon fiber and their photocatalytic degradation properties for dye compounds with different molecular size. *Catal. Commun.* **2008**, *9*, 1846–1850.
16. Ochiai, T.; Hoshi, T.; Slimen, H.; Nakata, K.; Murakami, T.; Tatejima, H.; Koide, Y.; Houas, A.; Horie, T.; Moritobe, Y.; *et al.* Fabrication of a TiO₂ nanoparticles impregnated titanium mesh filter and its application for environmental purification. *Catal. Sci. Technol.* **2011**, *1*, 1324–1327.
17. Li, J.; Chen, C.; Zhao, J.; Zhu, H.; Orthman, J. Photodegradation of dye pollutants on TiO₂ particles dispersed in silicate under UV-Vis irradiation. *Appl. Catal. B* **2002**, *37*, 331–338.
18. Kansal, S.K.; Singh, M.; Sud, D. Studies on photodegradation of two commercial dyes in aqueous phase using different photocatalysts. *J. Hazard. Mater.* **2007**, *141*, 581–590.
19. Ochiai, T.; Fujishima, A. Photoelectrochemical properties of TiO₂ photocatalyst and its applications for environmental purification. *J. Photochem. Photobiol. C* **2012**, *13*, 247–262.
20. Nakataa, K.; Fujishima, A. TiO₂ photocatalysis: Design and applications. *J. Photochem. Photobiol. C* **2012**, *13*, 169–189.
21. Pelaez, M.; Nolan, N.T.; Pillai, S.C.; Seery, M.K.; Kontos, P.F.G.; Dunlop, P.S.M.; Hamilton, J.W.J.; Byrne, J.A.; O’Shea, K.; Entezari, M.H.; *et al.* A review on the visible light active titanium dioxide photocatalysts for environmental applications. *Appl. Catal. B* **2012**, *125*, 331–349.
22. Yamashita, H.; Harada, M.; Tanii, A.; Misaka, J.; Nakao, H.; Anpo, M. Design of TiO₂ activated carbon filter systems by an Ionized Cluster Beam Method and their application for photocatalytic water purification. *Mol. Cryst. Liq. Cryst.* **2002**, *388*, 453–458.
23. Lin, L.-H.; Lee, H.-T. A new modified silicone–TiO₂ polymer composite film and its photocatalytic degradation. *J Appl. Polym. Sci.* **2006**, *102*, 3341–3344.

© 2013 by the authors; licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/3.0/>).