Photocatalytic performance of TiO$_2$ and Fe$_2$O$_3$ immobilized on derivatized polymer films for mineralisation of pollutants

M. R. Dhananjeyan, J. Kiwi and K. Ravindranathan Thampi*

Laboratory of Photonics and Interfaces (LPI), Swiss Federal Institute of Technology (EPFL), CH-1015 Lausanne, Switzerland. E-mail: ravindranathan.thampi@epfl.ch

TiO$_2$, Fe$_2$O$_3$ and Fe^{3+} have been immobilized on low cost polyethylene films containing anhydride anchoring groups showed enhanced mineralisation rates for chlorophenols and Orange II, compared to previously reported immobilized catalysts with rates which are comparable to or greater than catalytic suspensions.

Photocatalysis and photo-Fenton processes are able to break down many organic pollutants totally or partially so that cheaper biological processes can be used as a second stage to achieve complete mineralisation. Since photocatalysts are often applied as suspensions, costly problems associated with catalyst leaching, settling, flocculation and the need for eventual catalyst separation by filtration during post treatment, hinders their wide scale application in industry. In systems using photo-Fenton processes, removal of Fe ions after treatment is expensive. Therefore, catalyst immobilisation related research has attracted wide attention.[1] Simple coating[2,3] of the catalyst over glass, ceramics and polymers often lead to catalyst leaching and dissolution. There are reports on buoyant TiO$_2$-coated glass micro-bubbles[4] and polystyrene beads made by thermal treatment.[5] Immobilized catalysts may show reduced activity. Another problem generally noticed is the chemical attack by OH· radicals on the polymer substrates.[6] Photocatalysts immobilized on Nafion films[1] are expensive.

The present study was targeted to produce stable and efficient photocatalysts on low cost polymers, which could be used over many cycles without loss of activity. Chlorophenols and azo dyes like Orange II have been selected as model pollutants. The immobilized photocatalysts are based on TiO$_2$, Fe$_2$O$_3$ and Fe^{3+}.

In order to bind catalyst particles on the polymer, suitable anchor groups are required on the polymer surface. In this study, a polyethylene based anhydride-modified block copolymer (30 µm), specially prepared by E.I. Dupont de Nemours & Company, was used.

To prepare the immobilized catalyst,[7] the anhydride derivatized polyethylene film is washed with water before immersing in an aqueous suspension containing 5 g L^{-1} TiO$_2$ (Degussa P25). The suspension was sonicated 30 min prior to use. Together with the polymer, it is then heated to 75 °C for 1 h. The film was dried at 100 °C and washed with water to remove the loosely attached TiO$_2$ particles. For anchoring Fe$_2$O$_3$, α-Fe$_2$O$_3$ was used as the powder precursor and for Fe^{3+}, FeCl$_3$ (Fluka) was used as the starting compound.

Photocatalytic experiments were carried out using a 125 W medium pressure mercury lamp (2.5 × 10^{15} photons s^{-1}; λ = 360–390 nm) when TiO$_2$ is used and a Hanau Suntest lamp (80 mW cm^2 total intensity; 1.6 × 10^{16} photons s^{-1}; λ = 350–560 nm) for experiments using Fe$_2$O$_3$ and Fe^{3+} coated layers. The short UV radiation was filtered by the Pyrex wall of the reaction vessel. The decrease in the concentration of chlorophenols and Orange II was monitored by means of UV–VIS absorption spectroscopy and Total Organic Carbon (TOC) analyser. In control experiments with light, but without catalysts, the reactions did not proceed. Merckoquant paper® was used for estimating peroxide concentration.

Illumination of chlorophenol solutions (0.5 mM) in the presence of oxygen and TiO$_2$ coated films, at pH 6, results in rapid mineralisation of the organic compound. Fig. 1 shows the gradual decrease of TOC value of the chlorophenol solutions: 2-chlorophenol (Fig. 1A), 4-chlorophenol (Fig. 1B) and 2,4-dichlorophenol (Fig. 1C). 95% degradation was observed within 10 h for 2-chlorophenol. For both 4-chlorophenol and 2,4-dichlorophenol this time period was only 9 h. Control experiments showed no dark reaction on TiO$_2$ layers. The pseudo-first-order rate constants for the total mineralization of 2-chlorophenol (2-CP), using polymer–TiO$_2$ and powder suspensions (75 mg L^{-1} TiO$_2$), are 1.5 × 10^{-4} and 7.5 × 10^{-4} s^{-1}, respectively. For 4-CP, the rate constants are 1.7 × 10^{-4} s^{-1} for polymer–TiO$_2$ and 2.3 × 10^{-4} s^{-1} for the suspension (75 mg L^{-1}). For 2,4-DCP, the polymer catalyst showed a rate constant of 1.2 × 10^{-3} s^{-1}. With a higher amount of TiO$_2$ (1 g L^{-1}) suspension, the pseudo-first-order rate constant is determined as 1.5 × 10^{-3} s^{-1} for 2,4-DCP.

It is interesting to compare the results obtained with TiO$_2$ suspensions containing 25, 75, 500 and 1000 mg L^{-1}, with data using polymer–TiO$_2$, for the same reactions. With 75 mg L^{-1} suspension, the photocatalytic activity for 2-CP and 4-CP are
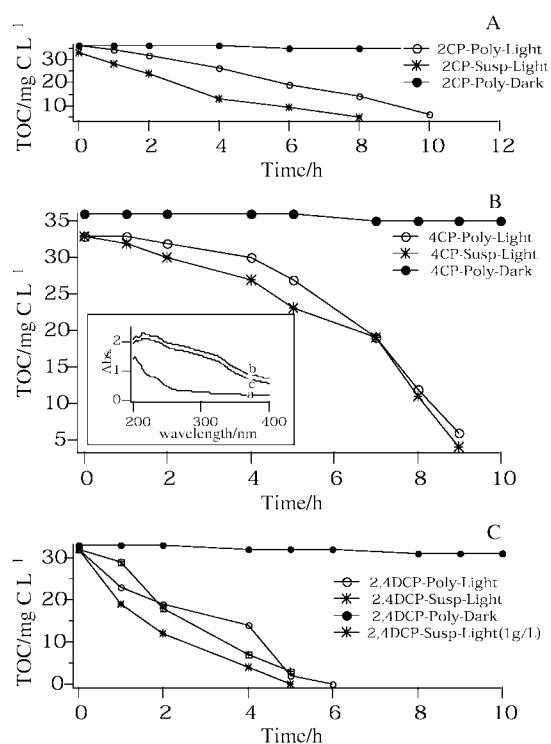
Fig. 1 Photocatalytic degradation of chlorophenols on TiO$_2$ coated polymer (size of sheet: 12 × 4 cm). A, [2-Chlorophenol]: 0.5 mM; poly: catalyst on polymer, susp: catalyst (75 mg L^{-1}) as a suspension. B, [4-Chlorophenol]: 0.5 mM; other descriptions as above. C, [2,4-Dichlorophenol]: 0.5 mM. The inset in Fig. 1B shows (a) the absorption spectra of polymer film, (b) TiO$_2$ coated film before use and (c) after six cycles.
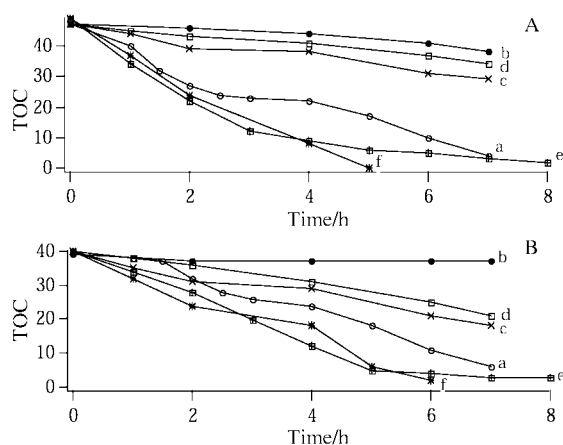
Fig. 2 Photo-Fenton degradation of 4-chlorophenol and Orange II on Fe_2O_3 polymer (size of sheet: 12×4 cm). A, [4-Chlorophenol]: 0.7 mM: (a): 4-CP-poly-Light; (b) Dark; [H_2O_2] = 0.01 M; (c): 4-CP-susp1-Light; [H_2O_2] = 0.001 M; Fe_2O_3 = 25 mg L^{-1} (d): 4-CP-susp2-Light; [H_2O_2] = 0.001 M; Fe_2O_3 = 75 mg L^{-1} (e): 4-CP-susp3-Light; [H_2O_2] = 0.01 M; Fe_2O_3 = 25 mg L^{-1} (f): 4-CP-susp1-Light; [H_2O_2] = 0.01 M; Fe_2O_3 = 75 mg L^{-1}; poly: catalyst on polymer, susp: catalyst as a suspension. B, [Orange II] = 0.2 mM; [H_2O_2] = 0.01 M. Curve (a): OrII-poly-Light; curve (b): Dark; [H_2O_2] = 0.01 M, other descriptions as in Fig. 2A.

comparable to the activity of the TiO_2 layer on the catalyst. By increasing TiO_2 to 0.5–1 g L^{-1}, complete mineralisation was obtained in *ca.* 6 h, compared to 9 h recorded for the TiO_2–polymer. However the amount of TiO_2 in the polymer is only 1.5 mg (48 cm^2 sheet size), corresponding to 37 mg L^{-1}. This shows that TiO_2 layers on the derivatized polymer are twice as efficient as a photocatalyst compared to the corresponding suspensions (3 mg in 40 mL dispersion). The reaction rates as well as the total mineralisation time of 2,4-DCP are similar when data of polymer catalyst and TiO_2 (1 g L^{-1} suspension) are compared, in which case the polymer catalyst is 25 times more active than the powder suspension. Since the polymer is transparent, it will not block light from reaching the photocatalyst during illumination. Furthermore, the TiO_2 particles do not mask each other from light and in a way are far more effectively dispersed than powder suspensions. When particles are suspended in water, besides causing shadows, they tend to aggregate causing inefficient surface utilization.

The inset Fig. 1B shows the change in light absorption by the TiO_2 polymer film before and after using six illumination cycles. We did not find any TiO_2 in solution when analysed by high resolution inductively coupled plasma spectrometry. The activity of the immobilized catalyst did not decrease during six runs. This confirms that the adhesion of TiO_2 is aided due to the chemical bond formed between the TiO_2 surface and the anhydride groups on the polymer. There is no significant change in the BET surface area of the loaded (1.45 m^2 g^{-1}) and unloaded sample (1.34 m^2 g^{-1}).

The TOC values never increased during the photodegradation run, indicating that the polymer is not chemically attacked by OH· radicals. Recycling experiments were carried out six times and no decrease in catalytic activity for the film was noticed.

The pH before the reaction was 6 and it decreased to 4.2 during the reaction. This is due to the production of HCl as a reaction product. It was also found that the H_2O_2 concentration, due to the formation and consumption of H_2O_2, was steady at *ca.* 0.5 mg L^{-1} throughout the reaction. The formation of H_2O_2 proceeds due to the capture of conduction band electrons by dissolved O_2.[8] There was no need to add H_2O_2 to effect the degradation of the organic compounds.

Illumination of aqueous solutions of 0.7 mM 4-chlorophenol and 0.2 mM Orange II in the presence of Fe_2O_3 coated polymer film and H_2O_2 results in mineralisation of the above compounds at pH 3. Fig. 2 shows the degradation of 4-chlorophenol (Fig. 2A) and Orange II (Fig. 2B) on Fe_2O_3 polymer film at pH 3. The

pseudo first-order rate constants for Fe_2O_3 polymer and Fe_2O_3 suspension are 4.6×10^{-4} and 8.7×10^{-4} s^{-1}, respectively.

To compare the catalyst loaded polymer and the corresponding powder suspension, four experiments with different weights of iron oxide and different concentrations of [H_2O_2] were also carried out. It was found that with 25 mg L^{-1} Fe_2O_3 susension and 1 mM H_2O_2 (4CP-susp1-Light, in Fig. 2A), the degradation was slower than with the polymer catalyst indicating that the production of OH· radical is not sufficient. When the amount of iron oxide is increased three times without simultaneously increasing H_2O_2 (4CP-susp2-Light), the rate of degradation was much slower. When [H_2O_2] is increased ten times, maintaining the same weight of iron oxide as 4CP-susp1-Light (4CP-susp3-Light), the rate of degradation also increased. This rate is comparable to that observed with the polymer catalyst and is also higher than 4CP-susp1-Light and 4CP-susp2-Light. In this situation, the Fe^{3+} and Fe^{2+} cycle proceeds and hence the OH· radical production is higher than in the other two cases. Here, the degradation of the compound is moderate and the activity is equal to that of the polymer catalyst. When both iron oxide and [H_2O_2] are increased three times and ten times respectively (4CP-susp4-Light), the rate of degradation is found to be faster than with the polymer catalyst. This confirms that an increased production of OH· radical and increased light absorption by the particle are both necessary to attain higher activity when the catalyst is in a suspended form.

The same trend was observed for degradation of Orange II and it takes 7 h to achieve 90% degradation as shown in Fig. 2B. No Fe^{3+} or Fe^{2+} was detected in solution, using thiocyanate as a complexing agent for Fe^{3+} and phenanthroline for Fe^{2+}. There was no change in the absorption spectra of Fe_2O_3 layers before and after six experimental cycles and this confirms the stability of the loaded Fe_2O_3 polymer film. The BET surface areas of the naked polymer film and Fe_2O_3 loaded film were measured and a noticeable surface area change was observed for the loaded polymer (2.77 m^2 g^{-1}) when compared to the free polymer (1.34 m^2 g^{-1}).

Illumination of aqueous solutions of 0.7 mM 4-CP and 0.2 mM Orange II in the presence of Fe^{3+} ions, loaded polymer film and H_2O_2 results in complete mineralisation of these compounds at pH 3 and no dark degradation was observed. The results were similar to those shown in Fig. 2A and B.

For comparison between polymer catalyst and the corresponding suspensions, experiments with homogeneous [Fe^{3+}] and [H_2O_2] solutions were carried out. By changing the Fe^{3+} and H_2O_2 concentrations, it was concluded that the polymer loaded film requires a lower amount of Fe^{3+} and H_2O_2, when compared to the amount required in homogeneous Fenton systems.

Stable immobilized TiO_2, Fe_2O_3 and Fe^{3+} on low cost derivatized polymer films do not compromise the catalytic activity of the powders. These composite catalysts are shown to be efficient for the photodegradation of industrial pollutants like chlorophenols and an azo-dye Orange II. The immobilized catalysts were shown to be stable in acidic as well as slightly basic (pH 9) media.

Notes and references

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