A new nano-TiO$_2$ immobilized biodegradable polymer with self-cleaning properties

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ABSTRACT

This study concentrated on the direct immobilization of anatase nano titanium dioxide particles (TiO$_2$, 10 nm particle size) *into* or *onto* a biodegradable polymer, polycaprolactone, by solvent-cast processes. The self-cleaning, namely photocatalytic properties of the produced materials were tested by photocatalytic removal of methylene blue as model compound and antimicrobial properties were investigated using *Candida albicans* as model microorganism. Produced TiO$_2$ immobilized polymer successfully removed methylene blue (MB, 1×10^{-5} M) from aqueous solution without additional pH arrangement employing a UV-A light (365 nm) source. Almost 83.2% of dye was removed or decomposed by 5 wt% TiO$_2$ immobilized *into* PCL (0.08 g) and removal percentage reached to 94.2% with 5 wt% TiO$_2$ immobilized *onto* PCL after a 150 min exposure period. Although removal percentage decrease with increased ionic strength and usage of a visible light source, produced materials were still effective. TiO$_2$ immobilized *onto* PCL (5 wt%) was quite effective killing almost 54% of *C. albicans* (2×10^6 CFU/mL) after only 60 min exposure with a near visible light source. Control experiments employing PCL alone in the presence and absence of light were ineffective under the same condition.

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1. Introduction

Polymers are very important materials being used to produce daily use items such as packaging, household appliances, building materials, paints, plastic sheets and laminates. Combining self cleaning properties would gain additional benefit. Biodegradable polymers are a class of polymer, which are decomposed by an enzymatic route and the products released to the environment do not cause negative effects. Often non-degradable polymers are substituted with biodegradable ones particularly in environmental applications, agriculture, food industry and medical use [1]. Polycaprolactone (PCL) is an example of a biocompatible, biodegradable, and non-toxic synthetic aliphatic polyester that is completely biodegradable inside the body after interaction with body fluids, enzymes, and cells, and therefore suitable for biomedical applications [2,3]. On the other hand, biodegradable polymers are preferred in tissue engineering which cells may be seeded, and which are introduced into a patient where the material gradually resorts, leaving behind a matrix of connective tissue and cells with the appropriate structural and mechanical properties [4,5]. These types of polymers are used to produce compostable bags, bottles for household cleaning materials since microbial decomposition and mineralization occurs when they are deposited into the environment.

Apart from other metal-oxide materials, titanium dioxide (TiO$_2$) particles have excellent photocatalytic properties and applications of this material have recently received great attentions owing to its chemical stability and high reactivity under UV light irradiation ($\lambda < 390$ nm). Produced hydroxyl radicals via charged holes (h$^+$) and excited electrons (e$^-$) are the main reactive species for oxidative/reductive degradation of a wide range of organic pollutants and details of the degradation process had been extensively discussed by Carp et al. [6].

Titanium dioxide particles can be utilized in the form of thin film which coated on a surface at nanometer scale. This is one of the most widely used materials in industrial applications since their unique dielectric, capacitor, transparent ferromagnetic and material properties serve in various applications such as corrosion protection, solar cells, gas sensors, and photocatalytic self-cleaning surfaces. Especially self cleaning properties being directly related to photocatalytic nature of TiO$_2$ particles are important to produce advance materials being used in everyday life.

Physical or chemical methods used to prepare thin films on glass, metal or ceramic substrates include sputtering, electrophoretic

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deposition, spray pyrolysis, thermal oxidation, chemical vapor deposition, and wet coating [6,7]. However, most of these techniques cannot be used for TiO_2 coatings on polymer substrates since they require high temperature calcination to obtain the desired photoactive anatase structure. The low surface energy of polymers and the lack of proper binding sites on the surface result in low adhesion leading to difficulty surface coating. To date, sol–gel and sputtering have been the main low temperature deposition techniques for coating TiO_2 nano particles on polymer substrates [7–13].

Direct immobilization of nano sized TiO_2 (n-TiO_2) could be a practical route for the preparation of these types of materials as the nano particles can be dispersed into the polymer or directly sprayed onto the surface during polymerization. Moreover, these materials could be used to remove contaminants from polluted water. Some procedures for the immobilization of TiO_2 into or onto polymers are already present in the literature. For example, photocatalyst has been prepared by coating Degussa P25 TiO_2 onto UVA transparent Plexiglass® (an acrylic polymer) however; the coating technique used was not described [14]. Chun et al. [15] reported that TiO_2 particles were deposited onto metal substrates (stainless steel, Cu alloy, Al alloy) and polymer substrates (PET, PMMA) by nano-particle deposition system (NPDS) at room temperature and low vacuum condition. Submicron size TiO_2 powders were sprayed through the supersonic nozzle and deposited at high deposition rate without thermal damage to the substrates. The scratch test was performed and particle penetration into stainless steel substrate was reported. NPDS was recommended as a coating technique for a wide number of applications using polymer substrates, including flexible displays and microfluidic devices. However, stability and durability of nanoparticles on the surface is questionable of this type of coating.

A novel photocatalyst based on Pt-doped titanium dioxide-coated magnetic poly(methyl methacrylate) microspheres was also prepared by Chen et al. [16]. However, this catalyst should be considered as a TiO_2 and polymer composite since proportions of TiO_2 was either immobilized into or onto polymer surface. A few other studies were published recently [17,18] and both materials were employed for antibacterial applications. These materials were only tested for antibacterial properties rather than photocatalytic activity.

In this study, we report the route for direct immobilization of anatase nano TiO_2 particles (10 nm particle size) *into* (direct addition of TiO_2 nanoparticles suspension into ε-caprolactone solution in chloroform) or *onto* (direct spraying TiO_2 nanoparticle suspension onto partly solidified polycaprolactone) a biodegradable polymer, polycaprolactone, by solvent-cast processes for producing materials that combine biodegradability and self cleaning properties. The aim of the study was to investigate the photocatalytic properties of the produced materials by the removal of the model compound, methylene blue, and to assess their antibacterial properties using *Candida albicans* as model microorganism. *C. albicans* is an eukaryotic organism (*ca.* 5–10 μm size) surrounded by a rigid cell wall composed mainly of glucan and chitin, which are associated with structural rigidity, and mannoproteins [19] and approximately 25–50 times larger than the bacteria. If a material is effective for killing *C. albicans* it should be highly active for all other less resistant microorganisms. Surface and structural analyses were also carried out to evaluate possible structural variations occurring during the treatment process. Both photocatalytic and antimicrobial improvement would be beneficial for the usage of this biodegradable polymer in packaging or medical applications since its environmentally friendly nature. Additionally this material can be used for removal or degradation of many pollutants present in various environments such as water and air.

2. Experimental

2.1. Preparation of n-TiO_2 immobilized PCL

Polycaprolactone, CAPA® 6800, was provided by Perstop Caprolactones (Cheshire, UK) as pellets and has a mean molecular weight of 80,000. Chloroform (Analytical reagent from Merck, Darmstadt) was used as the dissolving and casting solvent. For the immobilization of 10 nm sized n-TiO_2 powder (Aldrich, Darmstadt) *into* or *onto* PCL, two different solvent casting techniques were employed.

2.1.1. n-TiO_2 immobilized PCL (PCL-1)
Polycaprolactone (PCL) granules weighing 2.0 g were dissolved in 20 mL of chloroform. To another 20 mL portion of chloroform was added the required amount of n-TiO_2 and then vigorously mixed for 20 min. The amount of n-TiO_2 was varied; 1%, 5% and 10% relative to the solid weight of PCL. The PCL solution was then carefully mixed with the n-TiO_2 suspension and left to mix at high speed for a further 20 min. Aliquots of the PCL-TiO_2-chloroform suspension (10 mL) were cast into glass Petri dishes (75 mm diameter), these were loosely covered with a lid (diameter 80 mm) and placed in a fume hood at room temperature for a slow evaporation. The solvent dried polymer film (approx. 0.5 mm) was collected and dried for 48 h in a vacuum oven at room temperature. This material was defined as PCL-1.

2.1.2. n-TiO_2 immobilized on PCL (PCL-2)
PCL granules were dissolved and the n-TiO_2 powder was dispersed as above. The amount of n-TiO_2 was 5 wt% relative to the solid weight of PCL. For this solvent casting technique, only the PCL solution (10 mL aliquots) was cast into glass Petri dishes (75 mm diameter) and placed in a fume hood at room temperature for a slow evaporation. Before the PCL films were fully dried (approximately 20 min) the n-TiO_2 chloroform suspension was sprayed onto the partly solidified PCL film using a nanoparticle dispersion system (at 2–3 atm. pressure, spraying nanoparticle/chloroform suspension, SATA Minijet HVLP 3 90589). The n-TiO_2 treated PCL was then left to air-dry in a fume hood at room temperature. The air-dried polymer film was removed from the Petri dish and further dried for another 48 h in a vacuum oven. This material was defined as PCL-2.

2.2. Characterisation

The surface morphology of the polymer films was studied using a Nova NANOSEM-Philips scanning electron microscope. Attenuated total reflectance – Fourier transform infrared spectroscopy (ATR-FTRI) analysis of PCL and n-TiO_2 immobilized materials were carried out on a Nicolet Magna-IR 860 spectrometer with a Graseby-Specac Golden Gate™ sampling accessory. All films used in this study were handled and processed with due consideration for the differences between the polymer surfaces. The surfaces that had been in contact with glass Petri dishes during casting were denoted the GS surface, whilst those that had been exposed to air were denoted the AS surface [20]. Surface analyses were therefore performed on both the GS and the AS's, but n-TiO_2 immobilization was only applied to the AS. Surface deformation during exposure was tested using a UVC lamp emitting mainly 254 nm wavelength light, whereas photocatalytic experiments were performed using a UVA lamp emitting 365 nm. Thermogravimetric analysis (Seiko ExStar 6300 Model TG/DTA) was also performed on the samples before and after exposure.

2.3. Photocatalytic activity of n-TiO_2 immobilized PCL

Photocatalytic efficiencies were tested for the removal of aqueous solution of methylene blue (MB). A set of experiments were

designed to compare the photocatalytic actions of the n-TiO$_2$ immobilized PCL films.

Surface or structural variation studies of neat PCL and TiO$_2$ immobilized PCL (PCL-1 or PCL-2) were carried out in water with a UVC emitting lamp (254 nm, Spectroline ENF-260) at dye's natural pH. However, MB degradation processes were investigated at pH 2–10 range using a UVA emitting lamp (365 nm) or a visible light emitting sodium lamp. The solution pH was adjusted with 0.1 M NaOH or 0.1 M HCl solutions. A 5 mL portion of 1×10^{-5} M MB was placed in a quartz cell containing rectangular specimens (approximately 2×1 cm, 0.08 g, approx. 0.5 mm thick) cut with a scalpel blade. Both surface of the polymer was in contact with MB solution. The absorption of MB at 668 nm (UV–vis. Dr. Lange CADAS 200 Spectrometer) was monitored over 150 min in the presence and absence of light or polymer. Photoactivity tests of the films were also carried out in the presence of 4.3×10^{-3} M (250 ppm) NaCl solutions contacting both GS and AS.

2.4. Photokilling activity of n-TiO$_2$ immobilized PCL

C. albicans (an eukaryotic yeast, ATCC60193, 2×10^6 CFU/mL) suspended in normal saline was cultured in broth for 16 h, centrifuged, and washed in NaCl solution (0.9%) twice. The required number of microorganism was adjusted by dilution with the NaCl solution (0.9%).

A 5 mL portion of this solution was placed in a quartz cell containing 0.08 g of n-TiO$_2$ immobilized PCL film (PCL-2) and 10 μL portions were withdrawn at 15 min intervals during 60 min in the presence and absence of light. The 10 μL portions were directly cultivated on sabouraud dextrose agar plates. The plates were incubated for 24 h at 37 °C and the numbers of living colonies were counted to determine the number of viable cells expressed as the number of colony forming unit (CFU/mL) of *C. albicans*. The control sample was necessary to confirm the condition of the yeast, and act as a benchmark for the survival rate calculation. The method for testing the control sample was exactly the same as that of the n-TiO$_2$ immobilized PCL samples. Results are expressed as degradation percentage which was calculated from the number of colony forming units before and after treatment. All experiments were carried out in triplicate; particular attention was paid to those experiments which involved polymeric materials since these were cleaned with sterile water, dried and kept in sterile boxes until usage. All equipments (Petri dishes, glassware, pipettes and pipette tips) were sterilized by washing with ethanol and autoclaving at 170 °C for 1 h prior to use.

3. Results and discussion

3.1. Structural analysis n-TiO$_2$ immobilized-PCL

SEM analyses were carried out to determine the structural changes related to n-TiO$_2$ immobilization and UV exposure. Morphology of the polymeric materials (neat PCL, PCL-1 and PCL-2) before and after exposure to UV light for 48 h is given in Fig. 1.

It is noteworthy to indicate that the air surface appears to have a rougher surface this is due to the fact that chloroform is evaporated through the AS and not the GS. The SEM images collected before and after exposure (Fig. 1a–d) show that PCL does not undergo any major degradation and that both surfaces (AS and GS) still have fused spherule-like aggregates of approximately 100 μm in diameter. These observations are similar to the PCL films not exposed to UV light prepared by Tang et al. [20]. However, the morphology of the PCL-GS surface show a depressed surface structure after exposure compared to the more rounded aggregates prior to exposure. This might be due to some form of localized heating which

deforms/melts the surface during exposure as seen from the SEM image of GS at a higher magnification (Fig. 1c, at 20 μm). After long term UV treatment (1 week) slightly sheaf-like features were observed due to oxidative damage but this should be confirmed by other analysis techniques such as FTIR or Raman spectrometry [21].

The SEM analyses were repeated with 5% (w/w) n-TiO$_2$ immobilized PCL-1 and PCL-2, the findings are given in Fig. 2. SEM micrographs obtained from UV treated samples were very similar to non-treated PCL containing 5 wt% n-TiO$_2$ and are therefore not presented. It should be noted that the addition of n-TiO$_2$ into PCL resulted in an uneven surface containing aggregated TiO$_2$ particles and visible cracks and pinholes (due to a reduction in the adhesion of the spherules and incompatibility with TiO$_2$ and PCL) in both AS and GS surfaces (Fig. 2a and b). It looks like the spaces between the spherule-like agglomerates filled with TiO$_2$ particles. Incidentally, there are more of these 'cracks' on the GS rather than the AS this due to a sedimentation effect, i.e. the TiO$_2$ particles sedimenting to the bottom of the Petri dish.

Dispersion of nanoparticles could be more homogenous and use other techniques such as autoclaving the n-TiO$_2$/polymer solution or ultrasonic dispersion before casting can be used. However, spray nanodispersion of n-TiO$_2$ onto PCL substrate produce more homogenous and smooth PCL film and immobilization of n-TiO$_2$ particles on air surface is clear seen (Fig. 2c and d). This circle like islands seen on the surface (Fig. 2c) might be due to air pressure hit on polymeric surface or the tops of spherules that are devoid of TiO$_2$. The surface was checked after treatment and TiO$_2$ particles were still seen on the surface.

ATR-FTIR spectra were collected in the mid-infrared region (650–4000 cm^{-1}) with a resolution of 4 cm^{-1} and 64 scans (spectrums are not given). There was not any additional IR band corresponding to UV exposure of polymer for 48 h. Martins-Franchetti et al. [21] reported that UV irradiation had caused relatively large changes in the IR spectrum of the PCL film after 10 h UV exposure using a high potency ultraviolet irradiation directly to PCL surface. This was observed as a broadening of the strong band at 1727 cm^{-1} (carbonyl stretching group) together with a relative increase in intensity of the 1708 cm^{-1} band (also carbonyl stretching), the change was attributed to a change in polymer crystalinity resulting from irradiation.

Structural changes of PCL before and after UV or visible light exposure were also investigated by simultaneous thermo gravimetric and differential analysis (DTA-TGA, Fig. 3). Thermo gravimetric analysis revealed that polymer did not exhibit major deformation after a long term irradiation resulting a slight shifting of the melting point. In fact a 6 W UV lamp was used in our experiments and it seemed not to cause any degradation of PCL itself for a longer exposure time. This results indicates that PCL is stable during photocatalytic process unless contact to enzymes leading to its bio-decomposition.

3.2. Photocatalytic degradation of MB with PCL-1

Photocatalytic degradation of MB employing PCL-1 is given in Fig. 4. Degradation or removal percentages were calculated for 150 min exposure period and given in Fig. 5. Almost 36% of MB was degraded or bleached by UVA light after 150 min exposure. Initially, MB was adsorbed by PCL and only small fraction was absorbed or degraded by PCL itself. MB removal from the aqueous dye solution at pH 9 significantly increased with PCL-1. The percentage of n-TiO$_2$ was an important factor and best removal rates were obtained with 5 wt% n-TiO$_2$.

Photocatalytic processes are usually more effective in acidic pH ranges and therefore the same procedure was repeated at different pH between pH 2 and 10. The point of zero charge (pzc) of the TiO$_2$ (Degussa P25) is at pH 6.8 and TiO$_2$ surface is positively
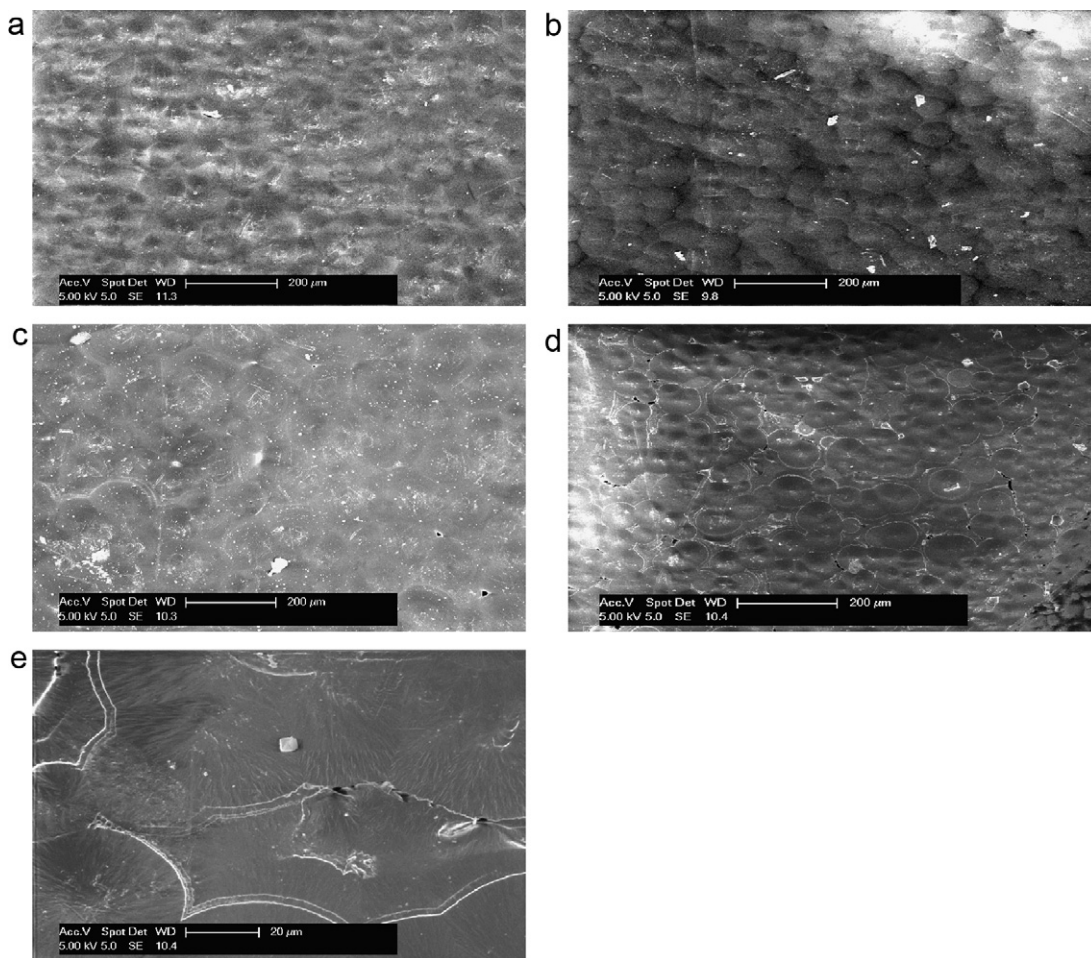
Fig. 1. Effect of UV exposure on the neat PCL surface morphology: (a) AS; (b); GS (c) AS/UV*; (d) GS/UV*. The scale bar shown in each micrograph is 200 μm in length and (e) PCL-GS/UV* at 20 μm length. *48 h UV exposure with 6 W lamp at λ = 254 nm.
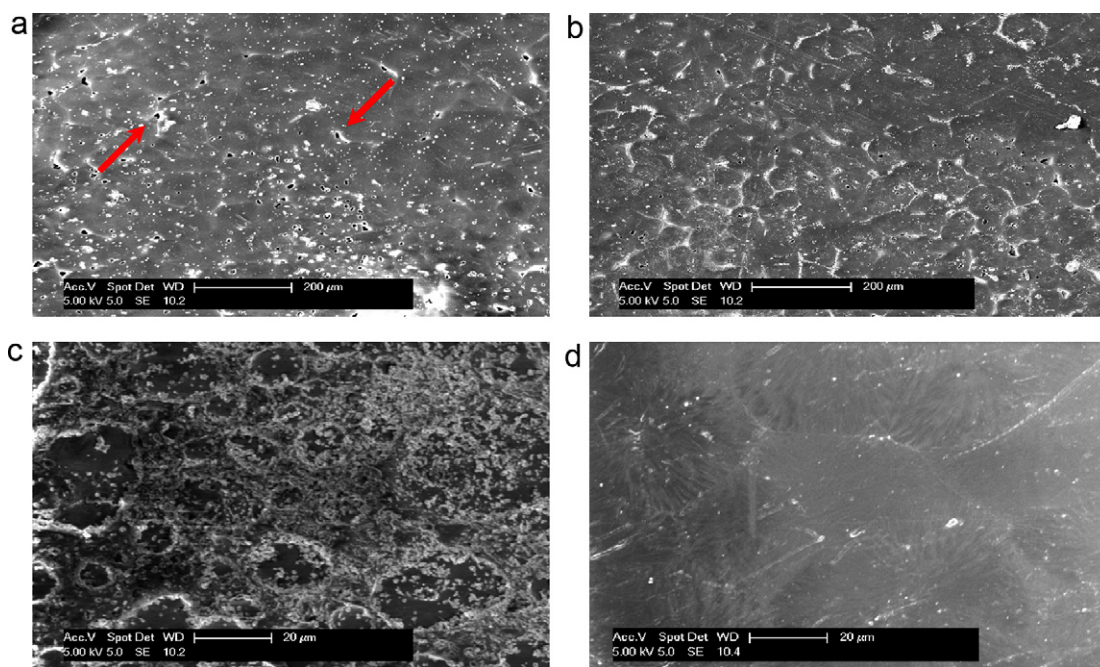

Fig. 2. The surface morphology of 5 wt% n-TiO$_2$ immobilized: (a) PCL-1 AS; (b) PCL-1 GS at 200 μm scale (white areas indicate aggregates of TiO$_2$ particles at the size of <20 μm) and (c) PCL-2 AS; (d) PCL-2 GS at 20 μm scale. Arrows shows cracks and pinholes.
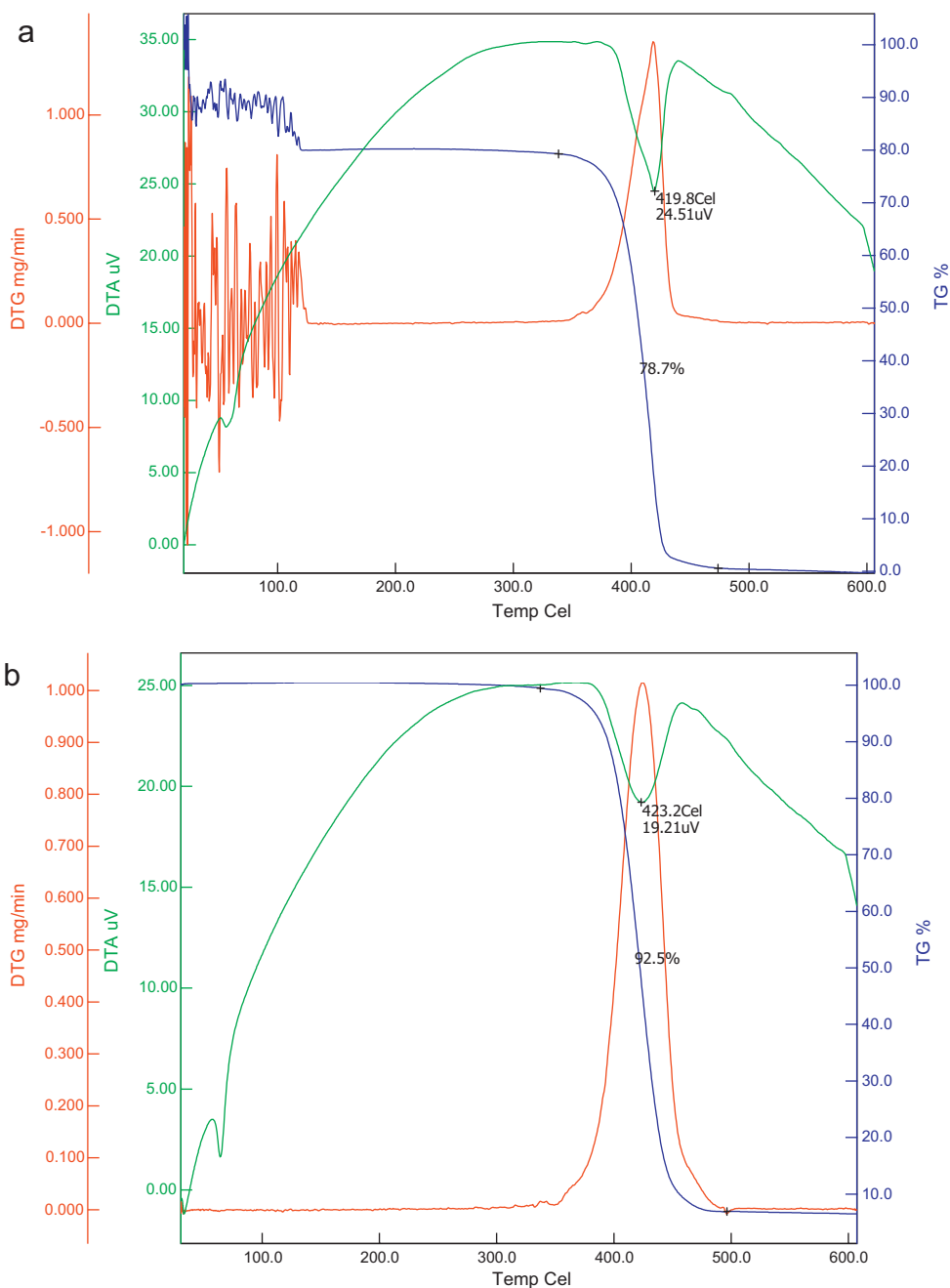
Fig. 3. Thermogravimetric and differential thermal analysis of (a) PCL (no UV) and (b) 5 wt% n-TiO$_2$ immobilized PCL (PCL-1) after UV irradiation for 48 h.
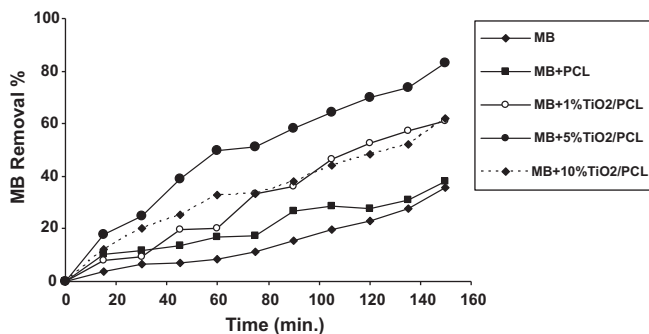

Fig. 4. Removal of MB at pH 9 (natural pH of 5 × 10^{-5} M MB) using a 365 nm light (sample mass is 0.08 g). Standard deviations were between 2 and 10% for all experiments and not included into figure.

charged in acidic media (pH < 6.8), whereas it is negatively charged under alkaline conditions (pH > 6.8). Since hydroxyl radicals can be formed by the reaction between hydroxide ions and positive holes the positive holes are considered as the major oxidation species at low pH [22]. Degradation or removal percentages were calculated for 150 min irradiation period and given in Fig. 5a. Removal efficiency at pH 9 was still the highest among the pH ranges studied. This is an advantage since removal or degradation processes do not require the commonly practiced, additional pH arrangement.

Photocatalytic action of the materials was also tested in the presence of 4.3 × 10^{-3} M (250 ppm) NaCl (Fig. 5b). In this case alteration of the ionic strength significantly inhibited both adsorption of the dye on the polymeric surface and the photocatalytic removal. Active sites of the surface were possibly occupied by ions and thus dye adsorption was prevented. In addition, the photocatalytic action of PCL-1 was tested employing a 40 W sodium light source emit-
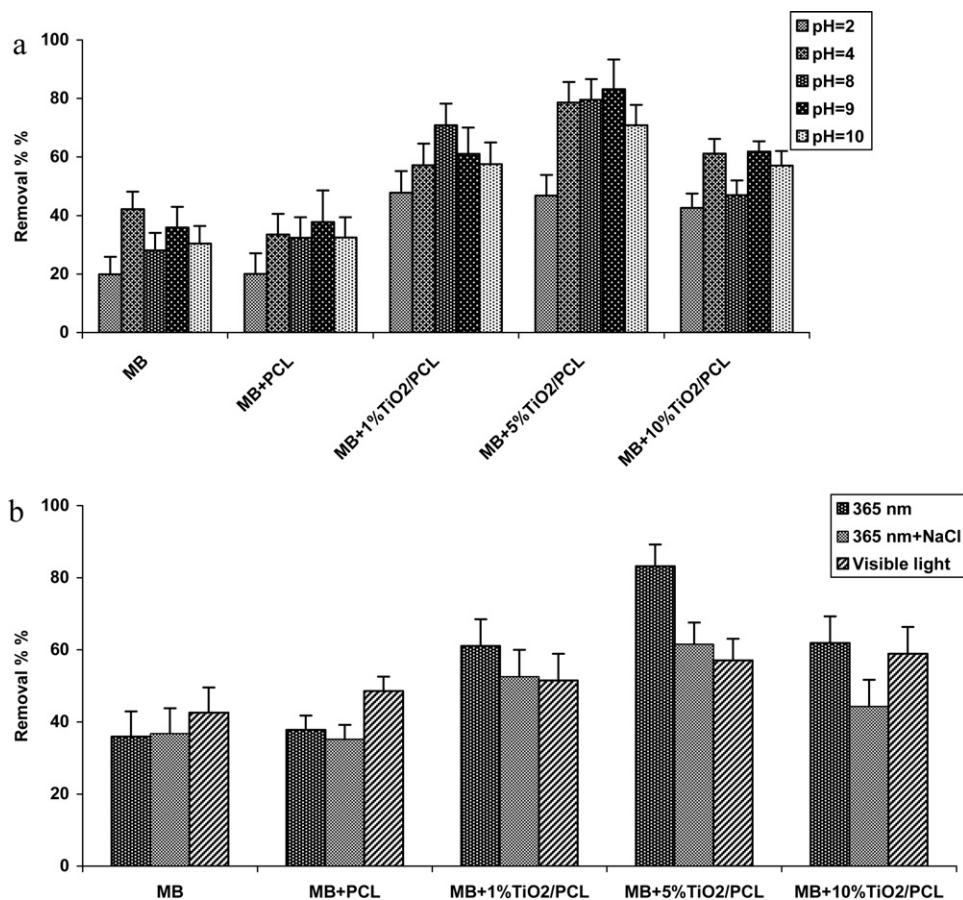
Fig. 5. Removal of 1×10^{-5} M MB with neat PCL and PCL-1 (a) at different pH after 150 min illumination with a 365 nm lamp; (b) at pH = 9 illumination with a 6 W 365 nm lamp in the presence of 4.3×10^{-3} M NaCl and 40 W sodium light emitting visible light ($\lambda \geq 400$ nm).

ting light over the whole visible range (400–750 nm). The removal percentages of MB after 150 min exposure are also given in Fig. 6 along with their removal rates in the presence of NaCl. Although the removal percentages of MB were lower than those using the 365 nm light, almost 59% of the dye was still removed either by adsorption of the dye or by photocatalytic degradation. After the treatment was completed the polymer samples were removed, dried in an oven (at 45 °C) and ATR-FTIR spectra were collected. The results revealed that MB was adsorbed by PCL since infrared bands corresponding to the functional groups of MB were observed. These bands were

lower in intensity or not present in the spectra obtained from the n-TiO_2 immobilized PCL samples indicating that MB was significantly or completely decomposed rather adsorbing on the PCL. However removal rates were lower than 365 nm exposure and not depending to percentage of TiO_2 in PCL.

3.3. Photocatalytic degradation of methylene blue with PCL-2

Experiments discussed above were also carried out with PCL-2 (TiO_2 was immobilized on air surface) and results are given in Fig. 6.

Immobilization of n-TiO_2 onto PCL produced improved MB removal percentages, especially for the sample containing 5 wt% TiO_2 since the removal percentage reached 94.2% after 150 min exposure with a 365 nm light. Naturally, immobilization of the nanoparticles on polymer surface lowers the mass transfer and this increases the rate of diffusion of the dye molecules to TiO_2 particles. As a result of this, dye molecules and active sites such as positive holes or hydroxyl radicals are more in contact. Moreover, for all the TiO_2 containing samples, the removal rates were higher, i.e. more MB was removed in shorter exposure periods. Percentage of immobilized TiO_2 seems to be an important aspect since overloading occupies all surface area including the small voids between the polymeric particles that increase the adsorption of MB.

3.4. Antibacterial properties

The reduction efficiencies of PCL-2 were checked for *C. albicans*, one of the most resistant microorganisms to conventional disinfection methods. Control experiments employing PCL alone in the presence and absence of light were also carried out under the same
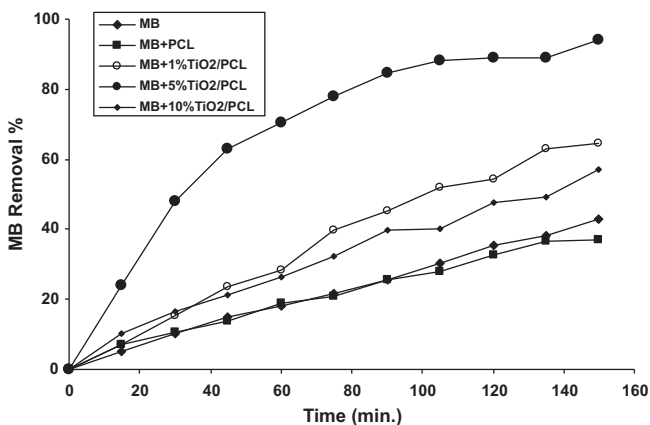

Fig. 6. Removal of MB with PCL-2 at pH 9 (natural pH of 1×10^{-5} M MB) using a 365 nm light (PCL mass is 0.08 g). Standard deviations were between 2 and 10% for all experiments and not included into figure.
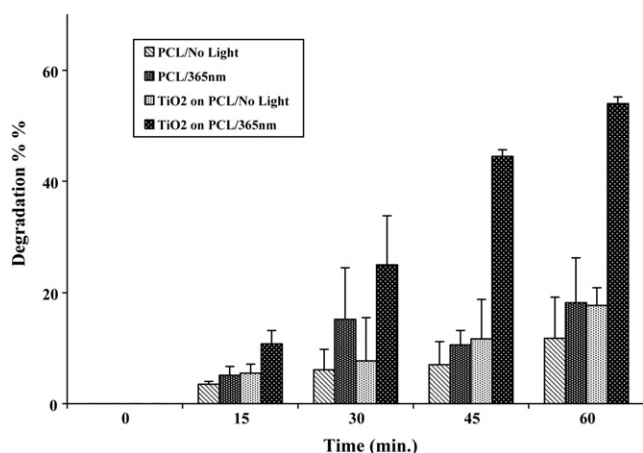
Fig. 7. Inactivation of *C. albicans* using PCL and 5 wt% n-TiO$_2$ immobilized PCL-2 in the presence and absence of light.

conditions. As seen from the results (Fig. 7), PCL-2 was quite effective killing almost 54% of *C. albicans* after only 60 min exposure with a near visible light source. However, only 18.2% of *C. albicans* was killed in the presence of polymer and light alone.

In one of the most important publications in the literature related to TiO$_2$, Kühn et al. [14] reported that the reduction efficiencies of TiO$_2$ coated Plexiglass decreased depending on the cell wall thickness. They found that *Gram-negative* microorganisms were killed easily, whilst *Gram-positive* microorganisms were more resistant. *C. albicans* was highly resistant to photocatalytic degradation due to its thick eukaryotic cell wall, but in our study, the number of living cells was reduced to nearly half that of the initial amount. This is a promising result especially when considering the simple preparation route and the incorporation of a biodegradable polymer.

4. Conclusions

Under the light of our findings, some important outcomes can be summarized. It was shown that it is possible to produce a biodegradable polymer containing n-TiO$_2$ particles in or onto PCL stimulated by UVA light. Produced materials successfully removed MB from aqueous solution without additional pH arrangement. Removal of the dye was still effective in the presence of high concentration salt. Spectroscopic and structural analyses reveal that TiO$_2$ immobilized PCL was resistant to structural changes and can be reused until its enzymatic degradation. The polymer which 5% TiO$_2$ immobilized onto PCL (PCL-2) provided high kill-rates for *C. albicans* indicating it might be more effective for less resistant micro organisms such as *E. coli*.

Acknowledgements

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