**Removal of textile dyes from water by TiO2 nanoparticles immobilized on**

**poly(ε-caprolactone) beads and foams**

DARKA MARKOVIĆ1, STOJA MILOVANOVIĆ2, MARIJA RADOIČIĆ3,

ŽELJKO RADOVANOVIĆ1, IRENA ZIZOVIC4,

ZORAN ŠAPONJIĆ3 AND MAJA RADETIĆ2[[1]](#footnote-1)

*1Innovation Center of the Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, Belgrade, Serbia*

*2Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, Belgrade, Serbia*

*3Institute of Nuclear Sciences “Vinča“, University of Belgrade, P.O. Box 522, Belgrade, Serbia*

*4Faculty of Chemistry, Wroclaw University of Science and Technology, Wybrzeze Wyspianskiego 27, 50-370, Wroclaw, Poland*

*Abstract*: This study discusses the possibility of colloidal TiO2 nanoparticles (NPs) immobilization onto poly(ε-caprolactone) (PCL) beads and foams which can be utilized for removal of textile dyes from water by photodegradation. PCL foams were fabricated by environmentally friendly treatment of PCL beads in supercritical carbon-dioxide. PCL beads and foams loaded with colloidal TiO2 NPs were used as photocatalysts for the removal of textile dyes C.I. Acid Orange 7 and C.I. Basic Yellow 28 from water under the illumination which simulated the sunlight. Unlike the PCL beads, the PCL foams provided complete discoloration of dye solution within 24 h of illumination. The PCL foams also exhibited excellent floatability that was maintained more than four weeks. Additionally, their photocatalytic activity was preserved within three repeated photodegradation cycles indicating that floating photocatalyst provided superior photocatalytic activity compared to non-floating PCL beads.

*Keywords*: Poly(ε-caprolactone); TiO2 nanoparticles; Dye photodegradation; Supercritical foaming.

RUNNING TITLE: TiO2 NANOPARTICLES IMMOBILIZED ON POLY(ε-CAPROLACTONE)

INTRODUCTION

Photocatalysis on semiconductor surfaces has gained much scientific attention due to their great potential for solving serious environmental problems. Among the metal oxide semiconductors, TiO2 nanoparticles (NPs) are the most widely used for degradation of organic pollutants. By absorbing the UV light (Eg≥3.2 eV) TiO2 NPs generate electron-hole pairs which migrate to the particle surface and react with surrounding molecules such as H2O and O2 producing very reactive radicals (OH·, O2-). These reactive oxygen radicals in combination with valence band holes successfully degrade a wide range of organic contaminants (phenols, pesticides, surfactants, dyes, etc.) and kill a various microorganisms (bacteria and viruses) in wastewater1-2. For the purposes of wastewater treatment TiO2 NPs are usually applied in the form of powder posing a problem of their post treatment separation. In order to overcome this drawback various substrates (glass, silica, zeolite, hydrogels, fibers, clay and activated carbon) have been explored as potential supports for immobilization of TiO2 NPs3-13. Recently, the floating substrates such as expanded perlite or polystyrene became very attractive since their floatability ensures maximum UV light utilization and oxygenation of photocatalyst, simple exploitation and post treatment recovery14-15. It should be stressed that most of these materials are non-biodegradable which means that after their exploitation the secondary pollution is generated. Hence, from environmental standpoint it would be desirable to replace these materials with biodegradable ones16 which are decomposed via enzymatic route without any toxic products. The papers related to biodegradable polymers as supports for TiO2 NPs are still scarce. It was reported that polycaprolactone film can be employed as a substrate for direct immobilization of TiO2 NPs and removal of methylene blue dye and 4-chlorophenol from water17-18. It was also reported that fibrous poly(L-lactide) textile material functionalized with nanosized ZnO was successfully employed for photocatalytic degradation of methylene blue and some reactive dyes.9

Taking into account the non-toxicity and biodegradability, of poly(ε-caprolactone) beads (PCLb) they were chosen as a substrate for immobilization of TiO2 NPs in this study. On the other hand, keeping in mind the advantages of floating photocatalysts, non-floatable PCLb were converted into form of floatable foam (PCLf). Intrigued with the studies reported by Fanovic & Jaeger20 and Ivanovic et al.21, which highlighted the applicability of compressed CO2 for PCL foaming, we decided to fabricate PCLf in supercritical CO2 (scCO2). Unlike conventional less environmentally friendly foaming agents (chlorofluorocarbons, hydrochloroflourocarbons and volatile organic components) scCO2 is non-toxic, chemically inert, non-flammable and allows working in a clean and safe environment22-23. Our first attempt for utilization of PCLf as a substrate for fabrication of floating photocatalyst was governed towards immobilization of commercial Degussa P25 TiO2 NPs24. The presence of rutile/anatase crystalline structure in these NPs made the process of dye photodegradation in water successful. However, in this study, we investigated the possibility of ffabrication of loating photocatalyst by immobilization of colloidal TiO2 NPs with anatase crystalline structure. In fact, we parallelly studied the photocatalytic behavior of TiO2 NPs immobilized on both PCLb and PCLf by evaluation of textile dyes (C.I. Acid Orange 7 and C.I. Basic Yellow 48) removal from aqueous medium under the light which simulated sun-like illumination.

EXPERIMENTAL

*Materials and Methods*

PCL beads (PCLb, Mn=80,000) were purchased from Sigma Aldrich, Germany. Commercial carbon dioxide of purity 99% was supplied by Messer-Tehnogas, Serbia.

The supercritical foaming of PCLb by CO2 was conducted in a high-pressure view cell (Eurotechnica GmbH, Germany) previously described in detail using the static method25. Experimental set-up is presented in Fig. 1. Individually wrapped beads in Teflon fabric were placed in the cell and heated to 40 ºC. Afterwards CO2 was introduced into the cell by opening valve V1. When pressure was elevated to 20 MPa using pump (Milton Roy, France) all valves were closed. After 2 h of PCLb exposure to scCO2, valve V2 was gradually opened and CO2 was released from the cell at the decompression rate of 0.5 MPa/min.

Colloidal TiO2 NPs were synthesized by acidic hydrolysis of TiCl4 26. All chemicals used in the synthesis were of analytical grade and used as received without any further purification. Milli-Q deionized water was used as a solvent. The solution of TiCl4 (Fluka) cooled down to -20 ºC was added drop-wise to cooled water (at 4 ºC) under vigorous stirring and kept at this temperature in the next 30 min. The pH of the solution ranged between 0 and 1, depending on the concentration of TiCl4. Slow growth of the particles was achieved by dialysis against water at 4 ºC until the pH of the solution reached 3.5. The concentration of TiO2 colloidal solution was determined from the concentration of the peroxide complex obtained after dissolving the particles in concentrated H2SO427. In order to improve the crystallinity and overall photocatalytic efficiency of generated TiO2 NPs, the colloid was thermally treated in reflux at 60 ºC for 16 h28. Mostly single crystalline, irregularly shaped TiO2 NPs with average dimensions of 6 nm were observed by HREM28. The electron diffraction pattern and Raman spectroscopy measurements confirmed the formation of anatase crystalline structure29.

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Fig. 1. Experimental setup for a high pressure foaming process: 1- view chamber, 2- light source, 3- pump, 4-cryostat, 5- camera.

PCLb and PCLf were dip-coated with colloidal TiO2 NPs according to the following procedure: 0.50 g of PCLb and PCLf were immersed in 55 mL of colloidal solution of TiO2 NPs (0.1 M). After 2 h long loading of PCLb and PCLf with TiO2 NPs, the samples were removed from the colloidal solution and dried at room temperature. In order to eliminate the excessive TiO2 NPs, the samples were rinsed (3×1 min and 1×5 min) with deionized water and dried at room temperature.

The morphology of the PCLf and the PCLf+TiO2 was analyzed by field emission scanning electron microscopy (FESEM, Tescan Mira3 FEG). The samples were coated with a thin layer of Au prior to analysis. Energy-dispersive X-Ray spectroscopy (EDX) of the PCLf with immobilized TiO2 NPs was performed using a JEOL JSM 5800 SEM with a SiLi X-Ray detector (Oxford Link Isis series 300, UK).

Fourier transform infrared (FTIR) spectra of the PCLf were recorded in the ATR mode using a Nicolet 6700 FTIR Spectrometer (Thermo Scientific) at 2 cm-1 resolution, in the wavenumber range from 500–4000 cm-1.

The photocatalytic activity of the PCLb+TiO2 and the PCLf+TiO2 samples was studied in aqueous solution of acid dye C.I. Acid Orange 7 (AO7, Bezema) and basic dye C.I. Basic Yellow 28 (BY28, Bezema). The structure of AO7 and BY28 are shown in Fig. 2a and 2b, respectively.

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(a) (b)

Fig. 2. The structure of dye C.I. Acid Orange 7 (a) and C.I. Basic Yellow 28 (b).

Photocatalytic degradation experiments were accomplished in accordance with the following procedure: 0.25 g of PCLb+TiO2 or PCLf+TiO2 were placed into 25 mL of AO7 or BY28 aqueous solutions (10 mg/L). The beaker with a sample was put in the water bath and it was illuminated by ULTRA-VITALUX lamp (300 W, Osram). This lamp provided sun-like irradiation. The distance between the lamp and the sample was set to 45 cm. Optical power was measured by R-752 Universal Radiometer Readout with sensor model PH-30, DIGIRAD and it was 30 mW·cm-2. The concentration of AO7 and BY28 solution was measured after 30, 60, 90, 120, 180, 240, 300, 360 and 1440 min of illumination at λmax=484 nm for AO7 dye and λmax=438 nm for BY28 dye using an UV-VIS spectrophotometer Cary 100 Scan (Varian). The percentage of dye removal (D) was calculated according to the following expression:

D= (1)

where: *C0*is the initial concentration of dye solution and *C* is the concentration of dye solution at studied time.

In order to evaluate a possible reusability of photocatalysts, described procedure was repeated twice.

The pseudo first order kinetic model was used to describe the process of water discoloration:

 (2)

where *C*0 is the initial concentration of dye solution (mg/L), *C* is the concentration of dye solution at time *t* (mg/L), *k* is the pseudo first order rate constant (1/min).

For the first order reaction the relation between the half life time (*t*1/2) and rate constant (*k*) can be calculated according to Eq. 3.30-31.

 (3)

RESULTS AND DISCUSSION

The surface morphology of the PCLf fabricated in scCO2 before and after TiO2 NPs immobilization was assessed by FESEM analysis. Unevenly distributed pores were detected on the surface of foams (Fig. 3a). Porous structure of the PCLf interior can be clearly seen in the inset of the Fig. 3a. The pore diameter varied in the range between 7.5 and 540 µm with an average size of 251±53 µm24. Obtained values are comparable with reported data21. Fig. 3b clearly reveals the presence of single and agglomerated TiO2 NPs on the PCLf+TiO2 surface. EDX analysis also confirmed the presence of TiO2 NPs on the surface of the foam (Fig. 4) i.e. certain picks assigned to Ti appeared in the EDX spectrum of the PCLf+TiO2 sample.

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(а) (b)

Fig. 3. FESEM images of surface of the PCLf (a) (inset: cross section of the PCLf) and surface of the PCLf+TiO2 (b) samples.

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Fig. 4. EDX spectrum of the PCLf+TiO2.

The photocatalytic activity of the TiO2 NPs immobilized on the PCLf and the PCLb was evaluated in aqueous solution of textile dyes AO7 and BY28 under the sun-like illumination. Our previous research indicated that the dye AO7 was not prone to photolysis while negligible photolysis occurred in the case of dye BY2824. Fig. 5a shows the percentage of AO7 removal from water in the presence of PCLb, PCLf, PCLb+TiO2 and PCLf+TiO2. The PCLb and the PCLf alone did not induce any dye removal. The PCLb+TiO2 and the PCLf+TiO2 removed 64% and 100% of dye AO7 within 24 h of illumination, respectively. Obviously, the PCLf+TiO2 ensured significantly faster dye removal rate. Namely, nearly 80% of the dye AO7 was removed within first six hours. Fig. 5b reveals that the dye BY 28 also did not photodegrade in the presence of the PCLb and the PCLf alone. The PCLf+TiO2 provided complete discoloration of dye solution within 24 h of illumination, while the PCLb+TiO2 provided the removal of only 66% of the dye BY28 for the same period of illumination. These results indicated that almost equivalent discoloration trend occurred for both dyes. A comparison of obtained results with our results related to the same substrates but loaded with commercial Degussa P25 NPs implied that both the PCLf and the PCLb with immobilized Degussa P25 NPs attained faster and more efficient removal of both investigated dyes from water under the equal conditions24. Just to illustrate, in the case of the PCLf+TiO2, 90% of dye AO7 and 100% of dye BY28 were removed already after six and three hours of illumination, respectively. Better photocatalytic activity of Degussa P25 NPs can be attributed to their specific anatase/rutile crystalline structure. Our TiO2 NPs consisted of only anatase phase. Namely, a synergetic effect appears between rutile and anatase in mixed phase TiO2 nanocomposites such as Degussa P25. The addition of rutile considerably enhances the photocatalytic activity of anatase phase29. In other words, when anatase and rutile phase are in the close contact, photo-excited electrons and holes are preferentially trapped in the anatase and rutile phases, inhibiting the unfavorable electron-hole recombination31-32. In spite of higher efficiency of these nanocomposite foams from photocatalytic point of view, the aggregation of Degussa P25 NPs on the surface and inside the PCLf make their detachment easier compared to the nanocomposite foam with immobilized colloidal TiO2 NPs.

The floatability of the nanocomposite foam is another very important issue that is worth discussing. It was observed that PCLf+TiO2 photocatalyst floated on the water surface throughout the 24 h long photodegradation experiment due to hydrophobic nature and the density of the PCLf of 289 kg/m3 24. As it was expected, floatability was not noticed in the case of the PCLb+TiO2 sample which has density of 1145 kg/m3. Taking into account this observation along with the results presented in Fig. 5, it could be concluded that the floating PCLf+TiO2 photocatalyst exhibited superior photodegradation activity compared to non-floating PCLb+TiO2 photocatalyst. Floatability of the PCLf+TiO2 sample ensured more efficient light utilization and maximum oxygenation which resulted in higher rate of radical generation and consequently in higher photocatalytic efficiency. Additionally, increased active surface area of the PCLf+TiO2 due to the presence of pores covered with TiO2 NPs facilitated the photodegradation process.

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(a)

**C:\Users\Darka\Desktop\PCL KOL\koloid prvi ciklus BY28_2.tif**

(b)

Fig. 5. The percentage of dye removal during the first cycle of illumination for the AO7 (a) and the BY28 (b) in the presence of different PCL samples.

All investigated samples remained white after the photodegradation experiments as can be seen in Fig. 6. White color of the PCLf+TiO2 sample implies that no residual dye remained in the nanocomposite foams after the first cycle of illumination.

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Fig. 6. Images of different PCL samples after the first cycle of illumination of dye

(AO7 and BY28) solutions.

In order to examine the possible reusability of the PCLf+TiO2 sample, photodegradation experiment was repeated twice. Fig. 7a and 7b reveal that the PCLf+TiO2 provided the complete discoloration of both dyes solutions within 24 h of illumination in the second and also in the third cycle. The photos in the Fig. 8 proved that the PCLf+TiO2 sample remained white after repeated illumination cycles. It should be noticed that the photocatalytic efficiency of the PCLb+TiO2 sample in the solution of BY28 increased with repetition of illumination cycles which can be ascribed to cleaning of the particles surface from impurities during the first photodegradation cycle28, 33. The results presented in Fig. 8 indicated that the PCLf+TiO2 floating photocatalyst could be successfully reused several times which is an imperative for the practical use.

It should be emphasized that the PCLf+TiO2 photocatalyst floated on the water surface even after the third illumination cycle. In fact, the floatability of the PCLf+TiO2 sample was sustained more than four weeks which was significantly longer compared to expanded perlite (10 days)15. Sustained floatability of the PCLf+TiO2 sample ensured its potential application as a floating photocatalyst.

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(a)

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(b)

Fig. 7. The percentage of dye removal during repeated cycles of illumination for the AO7 (a) and the BY28 (b) in the presence of PCLf+TiO2.

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Fig. 8. Images of the PCLf+TiO2 photocatalyst after repeated illumination cycles of dye

(AO7 and BY28) solutions.

It is well known that the pseudo first order kinetic model well fitted the photodegradation of different dyes in the presence of TiO2 NPs under UV illumination33, 34. Hence, the correlation coefficients *R2*, the pseudo-first order reaction rate constant *k* and the half-life *t*1/2 for dyes AO7 and BY28 in the presence of the PCLf+TiO2 sample were calculated (Eq. 2 and Eq. 3) and summarized in Table 1. The results from Table 1 demonstrate that the pseudo first order kinetic model also fits well the photodegradation process of dyes AO7 and BY 28. It is evident that the half-life calculated for both dyes is in good correlation with the experimental values presented in Fig. 7.

In order to investigate the possible chemical changes of the PCLf substrate during the photodegradation of the dye AO7 that might be induced by applied illumination and/or reactive oxygen radicals, the FTIR spectra of the PCLf+TiO2 sample before and after photodegradation experiments were recorded. The FTIR spectra of the PCLf+TiO2 before and after three repeated illumination cycles are shown in Fig 9. The strong band at 1720 cm-1 is related to C=O carbonyl stretching while the band at 1293 cm-1 corresponds to C-O and C-C stretching in the crystalline phase of the PCL18.

The results presented in Fig. 9 pointed out that the PCLf+TiO2 sample kept the chemical stability after three repeated photodegradation cycles. These results are in agreement with the results obtained by Sivlim et al.18 In contrast, Martins-Franchetti reported the changes in FTIR spectrum of the PCL films in the carbonyl region after 10 h of UV irradiation35. However, it is important to note that they applied higher dose of UV irradiation compared to the lamp in our study which simulated the sun light.

Table I. Kinetic data calculated for the photodegradation process of dyes

AO7 and BY28 in the presence of PCLf+TiO2 sample in aqueous medium

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Dye | Cycle | *R2* | *k*, min-1 | *t*1/2, min |
| AO7 | 1 | 0.999 | 0.0043 | 162 |
| 2 | 0.996 | 0.0027 | 258 |
| 3 | 0.987 | 0.0023 | 299 |
| BY28 | 1 | 0.995 | 0.0030 | 229 |
| 2 | 0.995 | 0.0040 | 172 |
| 3 | 0.995 | 0.0056 | 124 |

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Fig. 9. FTIR spectra of the PCLf+TiO2 before the first and after the third cycle of photodegradation of dye AO7.

CONCLUSION

The results presented in this study revealed that PCL foams could be successfully produced from PCL beads using supercritical CO2 as an environmentally friendly medium. The pore structure of the PCL foams was confirmed by FESEM analysis. The presence of TiO2 NPs on the surface of the foam loaded with TiO2 nanoparticles was proven by FESEM and EDX analyses. It was shown that such nanocomposite provided complete discoloration of textile dyes C.I. Acid Orange 7 and C.I. Basic Yellow 28 solutions within 24 h of exposure to sun-like illumination. Similar efficacy was obtained in two repeated illumination cycles. On the other hand, studied PCL beads were less efficient. PCL foams with immobilized TiO2 nanoparticles exhibited excellent floatability which was retained more than four weeks. Hence, good photocatalytic activity and sustained floatability of the PCL foams with immobilized TiO2 nanoparticles make them a viable candidate for practical use as a floating photocatalyst in treatment of textile industry waste water. The pseudo first kinetic model fitted well the photodegradation of both tested dyes in the presence of floating photocatalyst. This photocatalyst remained chemically stabile after three repeated cycles of illumination.

*Acknowledgements*: The financial support for this study was provided by the Ministry of Education, Science and Technological Development of Republic of Serbia (projects no. 172056 and 45020).

Извод

Уклањање боја за текстил из воде наночестицама TiO2 имобилисаним на перлама и пени од поли(ε-капролактона)

ДАРКА МАРКОВИЋ1, СТОЈА МИЛОВАНОВИЋ2, МАРИЈА РАДОИЧИЋ3,

ЖЕЉКО РАДОВАНОВИЋ1, ИРЕНА ЖИЖОВИЋ4,

ЗОРАН ШАПОЊИЋ3 И MAJA РАДЕТИЋ2

*1Универзитет у Београду, Иновациони центар Технолошко-металуршког факултета, Карнегијева 4, 11120 Београд, Србија*

*2Универзитет у Београду, Технолошко-металуршки факултет,*

*Карнегијева 4, 11120 Београд, Србија*

*3Универзитет у Београду, Институт за нуклеарне науке “Винча”,*

*П.П. 522, 11001 Београд, Србија*

*4Faculty of Chemistry, Wroclaw University of Science and Technology, Wybrzeze Wyspianskiego 27, 50-370, Wroclaw, Poland*

У овом раду је дискутована могућност имобилизације колоидних наночестица TiO2 на перлама или пени од поли(ε-капролактона) (PCL) које би се искористиле за уклањање боја за текстил из воде процесом фотодеградације. PCL пена је добијена еколошки прихватљивим третманом PCL перли у наткритичном угљеник(IV)-оксиду. PCL перле и пене су накнадно импрегниране колоидним наночестицама TiO2 и употребљене су као фотокатализатори за уклањање боја за текстил *C.I. Acid Orange 7* и *C.I. Basic Yellow 28* из воде при осветљењу које симулира сунчеву светлост. За разлику од PCL перли, PCL пене су обезбедиле потпуно обезбојавање раствора боје током 24 h осветљавања. PCL пена је такође показала одличну способност плутања која је очувана дуже од четири недеље. Фотокаталитичка активност пена је задржана таком три поновљена циклуса испитивања фотодеградације што указује да овај плутајући фотокатализатор показује супериорну фотокаталитичку активност у поређењу са неплутајућим PCL перлама.

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1. Corresponding author. E-mail: maja@tmf.bg.ac.rs [↑](#footnote-ref-1)