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Removal of textile dyes from water by TiO₂ nanoparticles immobilized on poly(ϵ -caprolactone) beads and foams

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Abstract: This study discusses the possibility of immobilization of colloidal TiO₂ nanoparticles (NPs) onto poly(ϵ -caprolactone) (PCL) beads and foams that could be utilized for the 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 the textile dyes C.I. Acid Orange 7 and C.I. Basic Yellow 28 from aqueous solutions (10 mg L⁻¹) under illumination that simulated sunlight. Unlike the PCL beads, the PCL foams provided complete discoloration of the dye solution within 24 h of illumination. The PCL foams also exhibited excellent floatability that was maintained for more than four weeks. Additionally, their photocatalytic activity was preserved within three repeated photodegradation cycles, indicating that the floating photocatalyst provided superior photocatalytic activity compared to the non-floating PCL beads.

Keywords: poly(ϵ -caprolactone); TiO₂ nanoparticles; dye photodegradation; supercritical foaming.

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 the degradation of organic pollutants. By absorbing UV light ($E_g \geq 3.2$ eV), TiO₂ NPs generate electron–hole pairs that migrate to the particle

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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 variety of microorganisms (bacteria and viruses) in wastewater.^{1,2} For the purposes of wastewater treatment, TiO₂ NPs are usually applied in powder form 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 the immobilization of TiO₂ NPs.^{3–13} Recently, floating substrates, such as expanded perlite or polystyrene, have become very attractive since their floatability ensures maximum UV light utilization and oxygenation of the photocatalyst, simple exploitation and post treatment recovery.^{14,15} It should be stressed that most of these materials are non-biodegradable which means that after their exploitation secondary pollution is generated. Hence, from environmental standpoint, it would be desirable to replace these materials with biodegradable ones¹⁶ that are decomposed *via* enzymatic routes without any toxic products. Papers related to biodegradable polymers as supports for TiO₂ NPs are still scarce. It was reported that poly(ϵ -caprolactone) film could be employed as a substrate for direct immobilization of TiO₂ NPs and removal of Methylene Blue dye and 4-chlorophenol from water.^{17,18} It was also reported that fibrous poly(L-lactide) textile material functionalized with nano-sized 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 (PCL_b), they were chosen as a substrate for immobilization of TiO₂ NPs in this study. On the other hand, bearing in mind the advantages of floating photocatalysts, non-floatable PCL_b was converted into the form of a floatable foam (PCL_f). Intrigued with the studies reported by Fanovic and Jaeger²⁰ and Ivanovic *et al.*,²¹ which highlighted the applicability of compressed CO₂ for PCL foaming, it was decided to fabricate PCL_f in supercritical CO₂ (scCO₂). Unlike conventional less environmentally friendly foaming agents (chlorofluorocarbons, hydrochlorofluorocarbons and volatile organic components) scCO₂ is non-toxic, chemically inert, non-flammable and enables working in a clean and safe environment.^{22,23} Our first attempt in the utilization of PCL_f as a substrate for the fabrication of a floating photocatalyst was governed towards immobilization of commercial Degussa P25 TiO₂ NPs.²⁴ The presence of both rutile and anatase crystalline structures in these NPs made the process of dye photodegradation in water successful. However, in the present study, the possibility of the fabrication of a floating photocatalyst by immobilization of colloidal TiO₂ NPs with the anatase crystalline structure was investigated. In fact, the photocatalytic behavior of TiO₂ NPs immobilized on both PCL_b and PCL_f were

in parallel studied by the evaluation of textile dyes (C.I. Acid Orange 7 and C.I. Basic Yellow 48) removal from aqueous medium under simulated sun-like illumination.

EXPERIMENTAL

Materials and Methods

PCL beads (PCL_b, $\bar{M}_n=80,000$ g mol⁻¹) were purchased from Sigma–Aldrich, Germany. Commercial carbon dioxide of purity 99 % was supplied by Messer-Tehnogas, Serbia.

The supercritical foaming of PCL_b by CO₂ was conducted in a previously described high-pressure view cell (Eurotechnica GmbH, Germany) using the static method.²⁵ The experimental set-up is presented in Fig. 1. Individually wrapped beads in Teflon fabric were placed in the cell and heated to 40 °C. Afterwards, CO₂ was introduced into the cell by opening valve V1. All valves were closed when the pressure had elevated to 20 MPa using the pump (Milton Roy, France). After 2 h of PCL_b exposure to scCO₂, valve V2 was gradually opened and CO₂ was released from the cell at the decompression rate of 0.5 MPa min⁻¹.

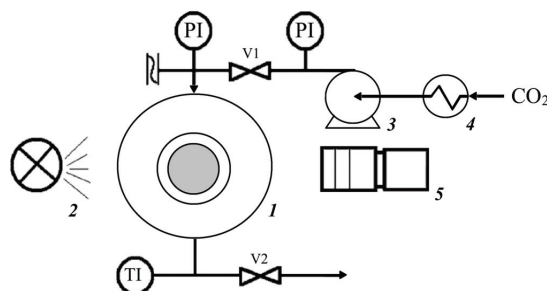


Fig. 1. Experimental setup for a high pressure foaming process: 1 – view chamber, 2 – light source, 3 – pump, 4 – cryostat, 5 – camera (TI – temperature indicator; PI – pressure indicator).

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 the solvent. TiCl₄ (Fluka) at –20 °C was added dropwise to cooled water (at 4 °C) under vigorous stirring and kept at this temperature for 30 min. The pH of the solution was zero. Slow growth of the particles was achieved by dialysis against water at 4 °C 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 H₂SO₄.²⁷ In order to improve the crystallinity and overall photocatalytic efficiency of the generated TiO₂ NPs, the colloid was thermally treated under reflux at 60 °C for 16 h.²⁸ Mostly irregularly shaped single crystals of the TiO₂ NPs with average dimensions of 6 nm were observed by HREM.²⁸ The electron diffraction pattern and Raman spectroscopy measurements confirmed the formation of anatase crystalline structure.²⁹

PCL_b and PCL_f were dip-coated with colloidal TiO₂ NPs according to the following procedure: 0.50 g of PCL_b (or PCL_f) was immersed in 55 mL of colloidal solution of TiO₂ NPs (0.1 M). After loading PCL_b (or PCL_f) with TiO₂ NPs for 2 h, 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 PCL_f and the PCL_f+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 PCL_f 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 PCL_f 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 PCL_b+TiO₂ and the PCL_f+TiO₂ samples was studied in an aqueous solution of the 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. S-1a and S-1b of the Supplementary material to this paper, respectively.

Photocatalytic degradation experiments were accomplished in accordance with the following procedure: 0.25 g of PCL_b+TiO₂ or PCL_f+TiO₂ was placed into 25 mL of AO7 or BY28 aqueous solution (10 mg L⁻¹). The beaker with a sample was placed in a water bath and shaken under a ULTRA-VITALUX lamp (300 W, Osram). This lamp provided sun-like irradiation. The distance between the lamp and the sample was set at 45 cm. The optical power was measured by an R-752 universal radiometer readout with a 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 λ_{max} = 484 nm for AO7 dye and λ_{max} = 438 nm for BY28 dye using a Cary 100 Scan UV–Vis spectrophotometer (Varian). The percentage dye removal (*D*) was calculated according to the following expression:

$$D = 100 \frac{C_0 - C}{C_0} \quad (1)$$

where: *C*₀ is the initial concentration of the dye solution and *C* is the concentration of the dye solution at the studied time.

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

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

$$\ln \frac{C_0}{C} = kt \quad (2)$$

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

For a 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}

$$t_{1/2} = \frac{0.693}{k} \quad (3)$$

RESULTS AND DISCUSSION

The surface morphology of the PCL_f fabricated in scCO₂ before and after immobilization of TiO₂ NPs was assessed by FESEM analysis. Unevenly distri-

buted pores were detected on the surface of the foams (Fig. 2a). The porous structure of the PCL_f interior can be clearly seen in the inset to Fig. 2a. The pore diameter varied in the range between 7.5 and 540 μm with an average size of 251 ± 53 μm .²⁴ The obtained values were comparable with reported data.²¹ The presence of mostly agglomerated TiO₂ NPs on the PCL_f+TiO₂ surface is revealed in Fig. 2b. EDX analysis also confirmed the presence of TiO₂ NPs on the surface of the foam (Fig. 3), *i.e.*, certain peaks assigned to Ti appeared in the EDX spectrum of the PCL_f+TiO₂ sample.

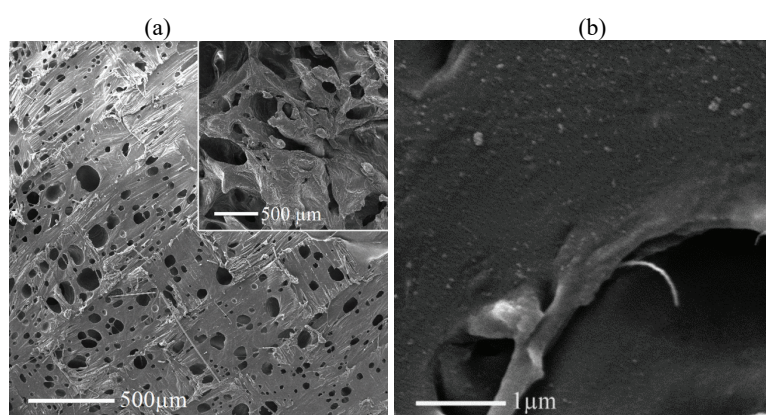


Fig. 2. FESEM images of the surface of PCL_f (a, inset: cross section of the PCL_f) and surface of the PCL_f+TiO₂ (b) samples.

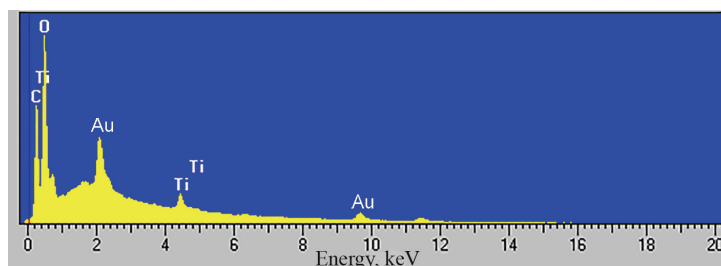


Fig. 3. EDX spectrum of PCL_f+TiO₂.

The photocatalytic activity of the TiO₂ NPs immobilized on PCL_f and PCL_b was evaluated in aqueous solution of textile dyes AO7 and BY28 under sun-like illumination. Previous research indicated that the dye AO7 was not prone to photolysis while negligible photolysis occurred in the case of dye BY28.²⁴ The percentage of AO7 removal from water in the presence of PCL_b, PCL_f, PCL_b+TiO₂ and PCL_f+TiO₂ are shown in Fig. 4a. PCL_b and PCL_f alone did not induce any dye removal. PCL_b+TiO₂ and PCL_f+TiO₂ removed 64 % and 100 % of dye AO7 within 24 h of illumination, respectively.

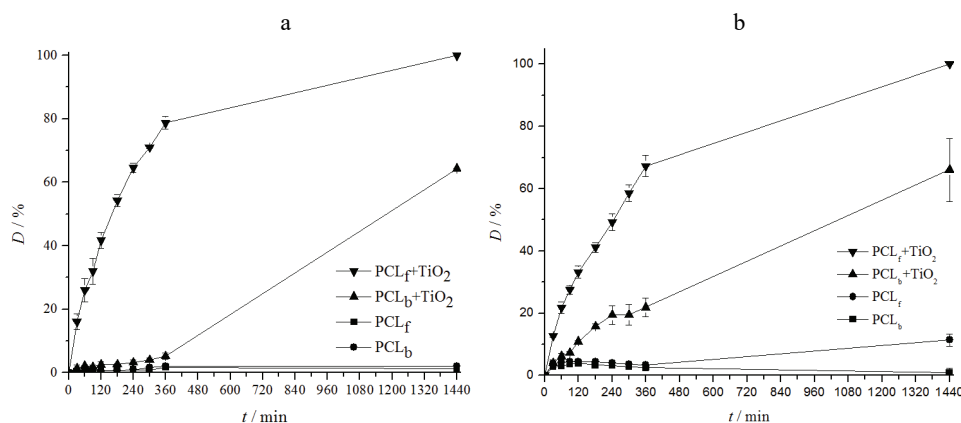


Fig. 4. The percentage of dye removal during the first cycle of illumination for AO7 (a) and BY28 (b) in the presence of different PCL samples.

Obviously, $\text{PCL}_f+\text{TiO}_2$ ensured a significantly faster dye removal rate. Namely, nearly 80 % of the dye AO7 was removed within the first six hours. As revealed in Fig. 4b, the dye BY 28 also did not photodegrade in the presence of PCL_b or PCL_f alone. $\text{PCL}_f+\text{TiO}_2$ provided for complete discoloration of the dye solution within 24 h of illumination, while $\text{PCL}_b+\text{TiO}_2$ provided for the removal of only 66 % of the dye BY28 for the same illumination period. These results indicated that almost equivalent discoloration trends occurred for both dyes. A comparison of the obtained results with the results related to the same substrates but loaded with commercial Degussa P25 NPs implied that both PCL_f and PCL_b with immobilized Degussa P25 NPs attained more rapidly and efficiently the removal of both the investigated dyes from water under the same conditions.²⁴ As an illustration, in the case of the $\text{PCL}_f+\text{TiO}_2(\text{Degussa P25})$, 90 % of dye AO7 and 100 % of dye BY28 were removed already after six and three hours of illumination, respectively. The better photocatalytic activity of Degussa P25 NPs can be attributed to their specific anatase/rutile crystalline structure. The present TiO_2 NPs consisted of only the anatase phase. Namely, a synergetic effect appears between rutile and anatase in mixed phase TiO_2 nanocomposites, such as Degussa P25. The presence of rutile considerably enhances the photocatalytic activity of the anatase phase.²⁹ In other words, when anatase and rutile phase are in close contact, photo-excited electrons and holes are preferentially trapped in the anatase and rutile phases, respectively, leading to better charge separation and consequently to inhibition of unfavorable electron–hole recombination.^{31,32} In addition, it was reported that the photocatalytic efficiency increases with crystallite size, which is larger in the case of Degussa P25.³³ In spite of higher efficiency of these nanocomposite foams from the photocatalytic point of view, the aggregation of Degussa P25 NPs

on the surface and inside the PCL_f makes 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 PCL_f+TiO₂ photocatalyst floated on the water surface throughout the 24 h long photodegradation experiment due to hydrophobic nature and the density of the PCL_f of 289 kg m⁻³.²⁴ As was expected, floatability was not noticed in the case of the PCL_b+TiO₂ sample that had a density of 1145 kg m⁻³. Taking into account this observation together with the results presented in Fig. 4, it could be concluded that the floating PCL_f+TiO₂ photocatalyst exhibited superior photodegradation activity compared to the non-floating PCL_b+TiO₂ photocatalyst. Floatability of the PCL_f+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, the increased active surface area of PCL_f+TiO₂ due to the presence of pores covered with TiO₂ NPs facilitated the photodegradation process.

All investigated samples remained white after the photodegradation experiments, as can be seen in Fig. S-2 of the Supplementary material. The white color of the PCL_f+TiO₂ sample implies that no residual dye remained in the nanocomposite foams after the first cycle of illumination.

In order to examine the possible reusability of the PCL_f+TiO₂ sample, the photodegradation experiment was repeated twice. Fig. 5a and b revealed that PCL_f+TiO₂ provided complete discoloration of both dyes solutions within 24 h of illumination in the second and in the third cycle. The photos in the Fig. S-3 of the Supplementary material proved that the PCL_f+TiO₂ sample remained white after repeated illumination cycles.

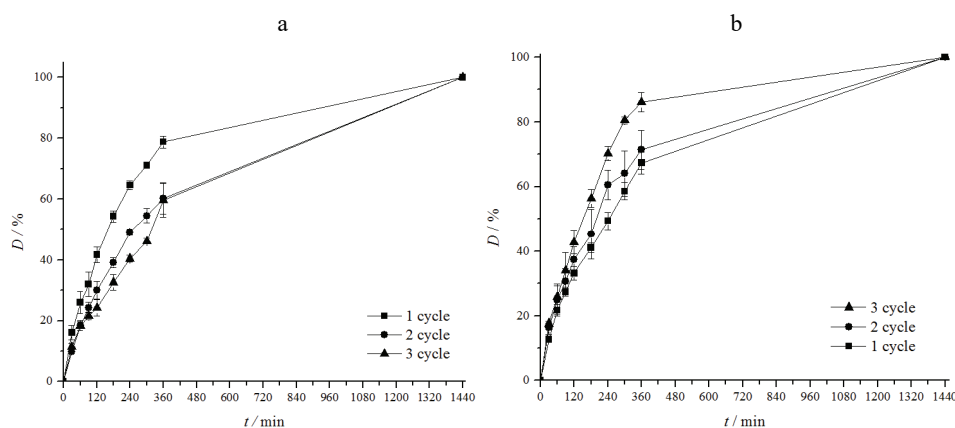


Fig. 5. The percentage dye removal during repeated cycles of illumination for AO7 (a) and BY28 (b) in the presence of PCL_f+TiO₂.

It should be noticed that the discoloration rate in the presence of the PCL_f+TiO₂ sample in the solution of BY28 increased with repetition of illumination cycles, which could be ascribed to cleaning of the surface of the particles from impurities during the first photodegradation cycle.^{28,34} In contrast, the discoloration rate in the case of the AO7 solution slightly decreased in the 2nd and the 3rd cycle, but complete dye removal was obtained after 24 h. The photographs presented in Fig. S-3 of the Supplementary material confirmed that the PCL_f+TiO₂ floating photocatalyst could be successfully reused several times, which is imperative for practical use.

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

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 illumination.^{34,35} Hence, the correlation coefficients R^2 , 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 PCL_f+TiO₂ sample were calculated (Eqs. (2) and (3)) and the results are summarized in Table I. The results from Table I demonstrate that the pseudo first order kinetic model also fits well the photodegradation process of dyes AO7 and BY28. It is evident that the half-life calculated for both dyes is in good correlation with the experimental values presented in Fig. 5. The rate constant decreased with repetition of illumination cycles in the case of AO7 whereas it increased for BY28.

TABLE I. Kinetic data calculated for the photodegradation process of dyes AO7 and BY28 in the presence of the PCL_f+TiO₂ sample in aqueous medium

Dye	Cycle	R^2	k / min^{-1}	$t_{1/2} / \text{min}$
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

In order to investigate the possible chemical changes of the PCL_f 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 PCL_f+TiO₂ sample before and after photodegradation experiments were recorded. The FTIR spectra of the PCL_f+TiO₂ before and after three repeated illumination cycles are

shown in Fig 6. 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 PCL.¹⁸

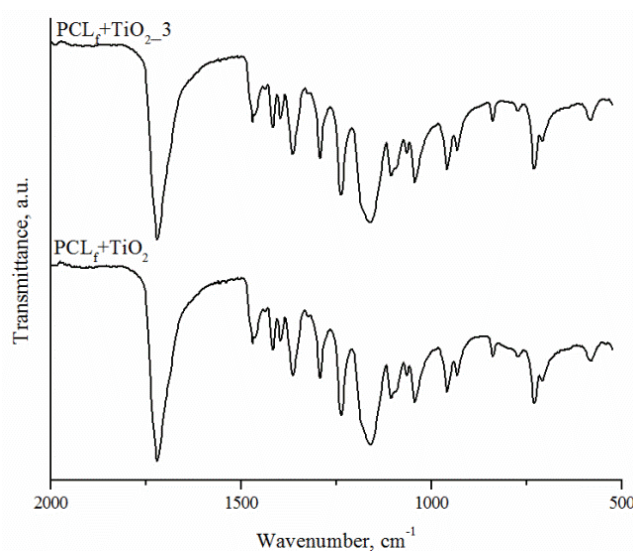


Fig. 6. FTIR spectra of PCL_f+TiO₂ before the first and after the third cycle of photodegradation of dye AO7.

The results presented in Fig. 6 indicated that the PCL_f+TiO₂ sample retained its 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 PCL films in the carbonyl region after 10 h of UV irradiation.³⁶ However, it is important to note that they applied higher dose of UV irradiation compared to the lamp in the present study in which simulated sun light was used.

CONCLUSIONS

The results presented in this study revealed that PCL foams could be successfully produced from PCL beads using supercritical CO₂ as an environmentally friendly foaming 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 a nanocomposite provided complete discoloration of textile dyes C.I. Acid Orange 7 and C.I. Basic Yellow 28 solutions (10 mg L⁻¹) 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 with immobilized TiO₂ were less efficient than PCL foams with TiO₂ nanoparticles. The PCL

foams with immobilized TiO₂ nanoparticles exhibited excellent floatability, which was retained for 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 wastewater. The pseudo first kinetic model fitted well the photodegradation of both tested dyes in the presence of the floating photocatalyst. This photocatalyst remained chemically stable after three repeated illumination cycles.

SUPPLEMENTARY MATERIAL

Additional data are available electronically at the pages of journal website: <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

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ИЗВОД

УКЛАЊАЊЕ БОЈА ЗА ТЕКСТИЛ ИЗ ВОДЕ НАНОЧЕСТИЦАМА TiO₂ ИМОБИЛИСАНИМ НА ПЕРЛАМА И ПЕНИ ОД ПОЛИ(ε-КАПРОЛАКТОНА)

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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 CO₂. 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 воденог раствора (10 mg L⁻¹) 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 таквом 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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