Photocatalytic degradation of Lissamine Green B dye by using nanostructured sol–gel TiO₂ films

Lidija Ćurković a,*, Davor Ljubas a, Suzana Šegota b, Ivana Bačić c

a Faculty of Mechanical Engineering and Naval Architecture, University of Zagreb, Ivana Lučića 5, 10000 Zagreb, Croatia
b Ruđer Bošković Institute, Bijenička 54, 10000 Zagreb, Croatia
c Forensic Science Centre Ivan Vučetić, Ministry of the Interior, Illica 335, Zagreb, Croatia

A R T I C L E   I N F O

Article history:
Received 9 November 2013
Received in revised form 20 January 2014
Accepted 24 March 2014
Available online 2 April 2014

Keywords:
Sol–gel TiO₂ films
Photocatalysis
Lissamine Green B
Atomic force microscopy

A B S T R A C T

Nanostructured sol–gel TiO₂ films were prepared on a glass substrate by means of the dip-coating technique with titanium tetraisopropoxide as a precursor. TiO₂ sols were synthesized with and without the addition of polyethylene glycol (PEG) as a structure-directing agent. The synthesized sol–gel TiO₂ were characterized by XRD, AFM, FTIR and Micro-Raman spectroscopy. The photocatalytic activity of the films was evaluated by the photocatalytic degradation of Lissamine Green B (LGB) dye (dissolved in water) as a model pollutant with the predominant irradiation wavelength of 365 nm (UV-A). It was found that the addition of PEG to the initial sol affects the surface morphology and the photocatalytic properties of prepared sol–gel TiO₂ films. AFM analysis confirmed the presence of nanostructured sol–gel titania films on the glass substrate. Roughness parameters (Rq, Rp, and Zmax) of the sol–gel TiO₂ film with the addition of PEG are higher than the parameters of the sol–gel TiO₂ film without the addition of PEG. The TiO₂ film prepared with the addition of PEG has a higher surface density (a larger active surface area) and better photocatalytic activity in the degradation of the LGB dye solution than the TiO₂ film prepared without the addition of PEG.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Many industries, such as dye, textile, cosmetic, leather, paper, food, plastics and pharmaceuticals industries, use dyes to colour their products. Many of these dyes could pose a serious threat to living organisms and they should be removed or degraded prior to discharge to the environment. Besides standard technologies for the removal of dyes, several new technologies, i.e. advanced oxidation processes (AOPs), have been developed. Among these AOPs, heterogeneous photocatalysis using TiO₂ as a photocatalyst has become an attractive and efficient technique with the potential for a complete destruction of undesirable contaminants (pollutants) in both the liquid and the gaseous phase by using solar or artificial light illumination [1–7]. This technique has the potential for the total mineralization of organic dyes, resulting in formation of CO₂, H₂O, and the corresponding mineral acids. Titanium dioxide or titania (TiO₂) occurs in three different crystalline phases: anatase (tetragonal), rutile (tetragonal), and brookite (orthorhombic). The most common phases for the use as photocatalysts are anatase and rutile.

TiO₂ can be used in the form of TiO₂ powder suspension (slurry) or it can be immobilised by different techniques on different substrates [8,9]. Immobilisation of TiO₂ on the adequate reactor walls eliminates the need of complicated separation of the photocatalyst from the treated water. Nowadays, the different deposition techniques are used: sol–gel, thermal treatment, pulsed laser deposition, reactive evaporation, physical vapour deposition (PVD), chemical vapour deposition (CVD), electrodeposition, sol-spray, hydrothermal deposition, etc. Among these techniques, the sol–gel technique offers a number of advantages: relatively low cost, low processing temperature, simple deposition, relatively simple control of composition, possibility of various forming processes, and ability to prepare nano-sized thin films and to produce fine structures [8–12]. Sol–gel films can be generally deposited by two methods – the dip coating and the spin coating technique [8,13]. The sol–gel process depends on many parameters, such as compositions and concentrations of alkoxides and solvents, catalysts, the sequence in which the components are added, and calculation temperatures. Sol–gel processing involves the hydrolysis and polycondensation of a precursor (e.g. metal alkoxide) and the subsequent formation of the gel, which results in a crystalline network structure after heat treatment.
In the process of the sol–gel deposition of titania films, one of the possible ways to produce a TiO$_2$ layer includes hydrolysis and the polycondensation of titanium alkoxides according to the following reactions:

$$\text{Ti(OR)}_4 + H_2O \rightarrow \text{Ti(OR)}_3OH + ROH \quad (1)$$

$$\text{Ti(OR)}_4 + \text{Ti(OR)}_3OH \rightarrow \text{Ti}_2\text{O}_2(\text{OR})_6 + \text{ROH} \quad (2)$$

The reaction stops with the inclusion of two water molecules:

$$\text{Ti(OR)}_4 + 2H_2O \rightarrow \text{TiO}_2 + 4ROH \quad (3)$$

The crystal structure and the surface morphology of films influence the photocatalytic efficiency of TiO$_2$ and it is very important to examine the surface. One of the tools for examining the thin film surface morphology at the nanoscale is atomic force microscopy (AFM). AFM is the most widely used tool not only for achieving the accurate three-dimensional reconstruction of the sample topography with atomic resolution within a short time but also for quantifying possible interactions at different interfaces. The second important reason for using this inexpensive technique is that there is almost no restriction in the structural analysis [14–18]. Other techniques for the characterisation of films that were used are X-ray diffraction (XRD), scanning electron microscopy equipped with an energy-dispersive X-ray analyzing system (SEM–EDX), ultraviolet–visible (UV–Vis) spectroscopy and Raman spectroscopy.

The aim of this research has been to prepare nanostructured sol–gel titania ceramic coatings (films), with and without the addition of PEG, for later use in photocatalytic oxidation experiments. The sol–gel dip-coating method was used for the deposition of TiO$_2$ coatings on a borosilicate glass substrate. Commercial dye Lissamine Green B (LGB) (also named Acid Green 50, Wool Green S, Food Green S or Green S) was used as a model pollutant and its photocatalytic degradation was monitored by total organic carbon (TOC) and UV–Vis measurements. This dye is used in industry to dye wool, silk, leather, etc. As a food dye, it is marked as an E number 142. It may cause allergic reactions and is one of the colorants that the Hyperactive Children’s Support Group recommends to be eliminated from the diet of children. Its chemical structure is indicated in Fig. 1.

2. Experimental procedure

2.1. Preparation of TiO$_2$ ceramic coatings

Nanostructured titania (TiO$_2$) coatings/films were deposited on a borosilicate glass substrate by the sol–gel process using the dip-coating method. Two types of borosilicate glass substrates were used: borosilicate glass cylinders (200 mm in height and 30 mm in diameter) and borosilicate glass plates with dimensions of $25 \times 30 \times 2$ mm. Two borosilicate glass cylinders were used as photoreactors and four borosilicate glass plates were used for the characterisation of films by means of AFM. The substrates were carefully cleaned prior to the process of deposition, using the procedure already described in [8].

For the preparation of colloidal solutions (TiO$_2$ sols), the following components were used:

1. titanium (IV) isoproxide ($\text{Ti(C}_2\text{H}_5\text{O}_2\text{)}_4$) – TIP as a precursor,
2. i-propanol ($\text{C}_3\text{H}_7\text{OH}$) – PrOH as a solvent,
3. acetylacetone (CH$_3$COCH$_2$CO$_2$H) – AcAc as a chelating agent,
4. nitric acid (HNO$_3$) – HN – 0.5 M as a catalyst,
5. polyethylene glycol, PEG (H(OCH$_2$CH$_2$OH)$_n$), M$_n$ = 5000–7000, as an organic/polymer additive.

All chemicals were analytical grade reagents. In the present study, two sols (colloidal solutions) were prepared: sol 1 and sol 2. Sol 1 was prepared by dissolving titanium isoproxide in i-propanol. A magnetic stirrer was used to continuously stir the liquid. Then, acetylacetone and nitric acid were added successively. Sol 1 was stirred vigorously for 2 h and after that it was sonicated for 30 min.

The molar ratio of these reactants was: TIP:PrOH:AcAc:HN = 1:3.063:0.015. Sol 2 was prepared using the same procedure as the one described for sol 1 with an exception, i.e. the addition of 2 g of polymer – PEG (average molecular weight of 6000). Borosilicate glass plates were dipped into the prepared sols at a rate of 10 mm/min, kept there for 10 min, and then removed at the same rate. Three layers TiO$_2$ films were deposited on substrates. The films were dried at 100 °C for 1 h prior to the deposition of the next layer. Also, sol 1 and sol 2 were poured into borosilicate glass cylinders, kept there for 10 min, and slowly poured out of them. The dipping process was repeated three times for both sols. After the deposition of the layers, the films on both substrates were annealed at 550 °C for 4 h.

2.2. Characterization of coatings

After the deposition of the sol–gel TiO$_2$ coating onto glass substrates, the remaining amount of solutions (sol 1 and sol 2) was dried at 60 °C for 24 h in order to produce dried gels and was calcined at a temperature of 550 °C for 4 h and prepared in the form of powder. These synthesized powders were analysed in terms of phase compositions of titania by means of X-ray diffraction (XRD) using a Philips PW 3040/60 X’Pert PRO powder diffractometer (Philips, Almelo, The Netherlands) with Cu Kα radiation (λ = 1.54056 Å) at 45 kV and 40 mA. Micro-Raman analyses were performed using Bruker SENTERRA Dispersive Raman spectrometer equipped with Olympus microscope. The Raman spectra of powder samples as well as of three layers TiO$_2$ films were analyzed at randomly selected points and under the same conditions – diode laser (AgGaS$_2$) operating at 785 nm, nominal laser power 100 mW, excitation power 10 mW, magnification 50×, aperture 25 × 1000 μm, spectral resolution 3–5 cm$^{-1}$, grating 1200l/mm, 5 s integration time. Spectra were recorded in frequency range 50–1350 cm$^{-1}$, and as a detector, a Peltier-cooled charged couple device (CCD) camera was used. FTIR spectra of powder samples were recorded on Bruker Tensor 27 FTIR spectrometer with ATR technique of the diamond cell. Spectra were collected in frequency range 600–4000 cm$^{-1}$ with 10 scans and spectral resolution 4 cm$^{-1}$. For manipulations of Raman and FTIR spectra, such as baseline correction (CRC Concave Rubberband Correction) and automatic determination of peak wavenumbers (Peak Picking), OPUS 7.0 software was used.

The surface topography and the roughness of the three-layer TiO$_2$ films were determined by using a Multimode AFM with a Nanoscope IIIa controller (Veeco Instruments Santa Barbara, CA) with a vertical engagement 125 μm scanner (JV). Contact mode imaging was performed under ambient conditions in air by using silicon tips (NP, Nom. Freq. 18 kHz, Nom. Spring constant of 0.06 N/m), at a scan resolution of 512 samples per line. The linear scanning rate was optimized between 1.0 and 2.0 Hz at a scan angle of 0°. Images were processed and analysed by means of the offline AFM NanoScope software, version 5.12r5. Particle dimensions of the granular microstructure of the TiO$_2$ thin film were determined by the Particle Analysis option within the AFM software. Roughness Analysis software option was used to perform roughness analyses on 2 × 2 μm$^2$ imaged surface area for each sol–gel TiO$_2$ film. Results are presented as the R$_{a}$, R$_{q}$ and the Z range values.

2.3. Photocatalytic experiments

The Lissamine Green B dye (LGB) purchased from Sigma–Aldrich (St. Louis, MO, USA), was selected as a model pollutant for the investigation of the photocatalytic activity of the prepared titania films. LGB solutions were prepared by dissolving the LGB powder in distilled water of MilliQ® quality. All experiments were carried out in the following 0.11 L borosilicate glass cylinder reactors (with 200 mm in height and 30 mm in diameter):

1. reactor 1, with a sol–gel TiO$_2$ film 1 without the addition of PEG,
2. reactor 2, with a sol–gel TiO$_2$ film 2 with the addition of PEG, and
3. reactor 3, a borosilicate glass cylinder without a TiO$_2$ film.

An UV-radiation lamp, model Pen-Ray CPQ 7427, with $\lambda_{\text{max}}$ = 365 nm (UV-A), manufactured by UVP, was placed in the middle of each reactor. The UV radiation reached the TiO$_2$ photocatalyst through the Lissamine Green B solution, causing

![Fig. 1. Chemical structure of the Lissamine Green B dye.](Image)
the photocatalytic oxidation process. The incident photon flux \( N_0 = 4.295 \times 10^{-6} \text{ einstein s}^{-1} \) was determined by actinometric experiments following the procedure described in [19].

Fig. 2 shows a scheme of the photoreactor.

The experiments of the degradation of LGB solution were carried out at a temperature of 25 ± 0.2 °C, with continuous purging with air (O₂), using three different conditions:

(i) under UV illumination in the absence of sol–gel TiO₂ film – reactor 3 (photolysis),
(ii) “in the dark” with sol–gel TiO₂ film 1 and TiO₂ film 2– reactor 1 and reactor 2 (adsorption) and
(iii) under UV illumination in the presence of sol–gel TiO₂ film 1 and TiO₂ film 2– reactor 1 and reactor 2 (photocatalysis).

The first set of experiments started with the initial concentration of Lissamine Green B of 7.3 mg/L, while the second set of experiments was carried out with different initial concentrations of Lissamine Green B (3.7 mg/L, 13.0 mg/L, 14.5 mg/L and 28.8 mg/L) under UV illumination in the presence of sol–gel TiO₂ film 2– reactor 2 (photocatalysis). These experiments were performed only in reactor 2 due to the confirmation from the first set of experiments that reactor 2 showed a better photocatalytic activity than reactor 1.

Before turning the UV lamp on, the solution was placed “in the dark” and covered with aluminium foil. The samples were taken from the reactor for analysis at particular intervals (15, 30, 45, 60, 90, and 120 min) and the remaining dye concentration was analysed with an UV-Vis spectrophotometer (HEWLETT PACKARD, Model HP 8430) at 633 nm by using a 1 cm quartz cell and a total organic carbon (TOC) analyser (Shimadzu, model TOC-VCPH).

For each condition, repetition tests were done to ensure reproducibility.

3. Results and discussion

3.1. XRD analysis

The crystalline structure of calcined TiO₂ samples was studied by the XRD measurement on powder samples of TiO₂. The TiO₂ sols were gelled and heat treated to be in the form of powder. The heating process applied was absolutely identical to that used for the TiO₂ film formation. Fig. 3A and B present X-ray diffractograms of the TiO₂ samples produced by the sol–gel technique with and without the addition of polyethylene glycol (PEG) to the initial sol, respectively. The results indicated that the TiO₂ synthesised from the initial sol 1 contains a higher amount of rutile phase than of anatase phase, while the TiO₂ sample synthesised from the initial sol 2 contains a higher amount of anatase phase than rutile phase.

3.2. Micro-Raman and FTIR spectroscopy

Micro-Raman spectroscopy was performed to identify crystalline phases of both TiO₂ powder samples and of thin films. Raman spectra are shown in Fig. 4A and B, respectively. Spectra are assigned and interpreted in accordance with the cited literature data [20–22]. Raman spectra of powder samples of sol 1 and sol 2 calcined at 550 °C confirmed the results obtained by X-ray diffraction. Namely, in both spectra anatase–rutile mixed phases were observed, and a higher amount of rutile phase was formed in sol 1 than in sol 2 (Fig. 4A). The typical bands of anatase phase appear around 143 (E₁g), 196 (E₁g), 396 (B₁g), 514 (A₁g, B₁g) and 638 cm⁻¹ (E₂g), while bands at 447 (E₁g) and 612 cm⁻¹ (A₁g) can be attributed to rutile phase. Unlike the powdered samples calcined at 550 °C, in Raman spectra of TiO₂ films calcined at this temperature no phase conversion to rutile is observed (Fig. 4B). Possible reason for these discrepancies could be non-uniform heating of the powder samples. As it is stated in literature, some grains that absorb maximum heat will grow faster than those that absorb less heat. Increasing of some anatase grains reduces defects at the grain boundaries and creates nucleation sites that facilitate the anatase to rutile phase transformation [20,23].

On the other hand, thin films are heated uniformly and there is no increase in anatase grains size that could be verified by comparison of full-widths at half-maximum (FWHM) of Raman bands (Table 1). Phonon confinement effect in nanocrystals is referred as one of the parameters that can cause broadening of the main Raman bands of the anatase phase as a result of decreasing of nanoparticles size [20–22,24]. Raman bands of the anatase phase of film 2 are slightly broader than those of the sol 2 powder sample.

Fig. 3. XRD patterns of the TiO₂ nano powder prepared (A) without the addition of PEG to the initial sol 1 and (B) with the addition of PEG to the initial sol 2.
(Table 1). Our observation of the increase of FWHM of considered bands in film 2 suggest that anatas crystallite size is lower in the film than in the powder sample.

These results are consistent with the literature data which indicate that the gradually transition from anatase to rutile phase in powdered samples occurs at a lower temperature than is the case for the thin films. Reported transition temperatures for the powdered samples are in the range of 400–600 °C [20,22,25,26], while transition from anatase to rutile phase in the thin films occurs at temperatures usually higher than 800 °C [24,27–29]. However, transition temperatures can vary due to different preparation methods, different techniques used [26] or even because of different number of layers at the film [30].

FTIR spectroscopy was used to show that the addition of polyethylene glycol (PEG) directly influence the formation of polymeric chain of TiO₂. Fig. 5 shows the infrared transmittance spectra of TiO₂ powder (sol 1) and TiO₂/PEG powder (sol 2) calcined at 100 °C.
The spectra show significant differences, primarily due to the bands that originate from the added PEG (sol 2). In the range from 3640 to 3040 cm\(^{-1}\) the spectra show the presence of O–H stretching vibrations. In sol 1 spectrum in this range a broad band with one pronounced maximum at 3213.0 cm\(^{-1}\) that probably originates from Ti–O–H bonds is present as well as from absorbed water [24,31]. In this region of sol 2 spectrum one more bad resolved maximum at 3446.1 cm\(^{-1}\) was observed. Djaoued et al. [28], based of knowledge that PEG molecules adsorb exothermically onto TiO\(_2\) oligomers, have been attributed this band to the stretching vibration of hydrogen bonds between oxygen atoms in the PEG and hydroxyl groups on the TiO\(_2\). This band was not observed in sol 1 spectra as well as in spectra of pure PEG (not shown in Fig. 5). In both spectra, vibrational bands at 2980 cm\(^{-1}\) and around 2885 cm\(^{-1}\) are attributed to asymmetric and symmetric stretching of the C–H groups in the structure of the sol 1 and sol 2. Bending vibrations that correspond to alkyl groups (\(\delta{\text{CH}}_3\), \(\delta{\text{CH}}_2\)) are observed in the range 1460–1340 cm\(^{-1}\), and together with the absorption bands around 1580 and 1530 cm\(^{-1}\), are characteristic for acetylated groups that are bound to titanium [31,32]. Unlike the sol 1, in the sol 2 spectrum at 1245.0 and 1099.5 cm\(^{-1}\) strong bands that originate from \(\nu{\text{C–O–C}}\) bonds of PEG are present, while the broad band at 1099.5 cm\(^{-1}\) is due to the ether linkage [24,28,31,33]. Absence of the absorption peak at 1099 cm\(^{-1}\) in sol 1 spectra could be explained in accordance with report of Huang et al. [32]. They reported that peak from Ti–O–C (1097 cm\(^{-1}\)) disappears due to hydrolysis and formation of Ti–O–H bending, which was during polycondensations between PEG and TiO\(_2\) oligomers substituted by Ti–O–C bending. Another evidence of the polycondensations between the chain of TiO\(_2\) and PEG is the absence of absorption peak from \(\nu{\text{C–O–C}}\) (around 870 cm\(^{-1}\)) in IR spectra with PEG (sol 2) which is present in sol 1 [34]. Significant vibrational band that appears around 650 cm\(^{-1}\) corresponds to TiO\(_2\) modes in the anatase phase [31].

### 3.3. AFM analysis of sol–gel TiO\(_2\) films

Particle size distribution of TiO\(_2\) films is one of the key factors responsible for their photocatalytic efficiency [35]. Their well-defined crystallinity and the size of TiO\(_2\) particles can be obtained by the AFM analysis. Fig. 6A and B shows surface topography three-layer sol–gel TiO\(_2\) film 1 and film 2.

The AFM analysis of the TiO\(_2\) film 1 and film 2 on the glass substrate shows granular microstructures containing regular, almost monodispersal spherical particles. The AFM image analysis also gives the value of surface roughness as well as grain size distribution. The values of roughness parameters of both investigated films are presented in Table 2.

The \(R_a\) values of the three-layer sol–gel TiO\(_2\) films without and with addition of PEG are 2.06 nm and 4.38 nm, respectively. The \(R_q\) values were similar to those (2–4 nm) reported in the literature [36–38], indicating good homogeneity of the TiO\(_2\) particles on the surface [36]. In addition, the minimum, the maximum, and the mean TiO\(_2\) grain size of both investigated films are listed in Table 3.

The addition of a small amount of PEG to the TiO\(_2\) film 2 significantly changes the surface morphology as well as roughness parameters. The roughness parameters (\(R_a\), \(R_q\) and \(Z_{\text{max}}\)) are higher in comparison to the values found in the film 1 without PEG and these findings are in agreement with the results reported in [39–41].

The surface roughness seems to correlate to the grain size distribution of TiO\(_2\) film as shown in Table 2. With addition of PEG in the film, the mean grain size decreased from (65.2 ± 5.1) nm to (28.3 ± 2.6) nm indicating the increase of the grain number at the investigated surface area, e.g. the surface density from 62.8 to 171.7 \(\mu\text{m}^2\), as shown in Table 2. Consequently, since the film has a larger active surface area, the photocatalytic activity of the modified film with addition of PEG could be much better.

### 3.4. Photocatalytic degradation of LGB dye solution

Fig. 7 shows the time-dependent UV–Vis spectra of LGB aqueous solution with a concentration of 7.3 mg L\(^{-1}\) as a starting solution during the photocatalytic oxidation process in reactor 2. It is clear from this figure that the intensity of the absorption peaks decreases with the time of UV-radiation exposure, which implies that the LGB is degraded. The initial pH value of the solution was 7.20, and after 120 min it decreased to the values between 5.50 and 5.90. Experiments performed “in the dark” confirmed that the effects of adsorption of LGB on the surface of TiO\(_2\) catalyst film were negligible in the overall colour removal process in comparison with the photocatalytic oxidation process (Fig. 7).

The obtained results shown in Fig. 8 confirm that the duration of the UV exposure and the presence of the TiO\(_2\) films influence

![Fig. 6. Surface topography of the (A) sol–gel TiO\(_2\) film 1 with three layers and (B) sol–gel TiO\(_2\) film 2 with three layers.](image-url)
the degree of LGB dye photodegradation. The direct photolysis of the LGB with UV-A radiation (reactor 3) resulted in a lack of degradation.

TOC removal in comparison to the absorbance removal of the dye solution in reactor 2 is shown in Fig. 9.

The experimental results indicate that the removal of colour and the dye itself was more rapid than the removal of TOC of the dye solution. This observation indicates that the total mineralisation of the dye solution is not completed after 120 min of the radiation exposure and the degradation products of the dye are still present in the solution; therefore, for their total removal the period of exposure should be prolonged.

In general, the dye photocatalytic decolourisation rates closely follow the Langmuir–Hinshelwood (L–H) type kinetic model given by the following equation [8,42,43]:

\[
\frac{dc}{dt} = \frac{kKC}{1 + KC}
\]

where \( C \) is the LGB concentration (mg/L) at a time \( t \) (min), \( k \) is the reaction rate constant (mg/L min), and \( K \) is the adsorption coefficient of LGB (L/mg). After integration, Eq. (4) is transformed into:

\[
t = \frac{1}{KK} \ln \left( \frac{C_0}{C} \right) + \frac{1}{k} \left( C_0 - C \right)
\]

When the initial dye concentration \( (C_0) \) is in the order of ppm, the equation can be simplified to [42,43]:

\[
- \ln \left( \frac{C_0}{C} \right) = k' t
\]

where \( k' \) is the pseudo-first order rate constant in min\(^{-1}\).

The pseudo-first order rate constant \( k' \) from Eq. (6) is evaluated through the linear regression of \(-\ln(C/C_0)\) versus \( t \) (not shown here).

The corresponding values of the pseudo-first order rate constant \( k' \) as well as the determination coefficient \( R^2 \) are given in Table 4. The results show that the photocatalytic decolourisation of the LGB dye can be described by the pseudo-first order kinetic model.

The rate constants were calculated to be \( 16.5 \times 10^{-3} \) and \( 42.9 \times 10^{-3} \) for experiments performed in reactor 1 and reactor 2, respectively (Table 4). The obtained values of the determination

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Effect of addition of PEG to grain size distribution of TiO(_2) film.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sol gel TiO(_2) film</td>
<td>Mean grain size (nm)</td>
</tr>
<tr>
<td>Film 1, 3 layers</td>
<td>65.2 ± 5.1</td>
</tr>
<tr>
<td>Film 2, 3 layers</td>
<td>28.3 ± 2.6</td>
</tr>
</tbody>
</table>

Fig. 7. UV–Vis spectra of LGB solution after a photocatalytic treatment in reactor 2: (a) starting concentration of LGB in the aqueous solution of 7.3 mg L\(^{-1}\), (b) after 15 min (c) after 30 min, (d) after 45 min, (e) after 60 min, (f) after 90 min, and (g) after 120 min of photocatalytic oxidation.

Fig. 8. Decolourisation of Lissamine Green B by sol–gel TiO\(_2\) films under UV-A irradiation and initial dye concentration of 7.3 mg L\(^{-1}\).

Fig. 9. Colour and TOC removals of Lissamine Green B by the sol–gel TiO\(_2\) film 2 under UV-A (365 nm) irradiation and initial dye concentration of 7.3 mg L\(^{-1}\) in reactor 2.
coatings as the only films and that reduces the degradation rate.

The film prepared with the addition of PEG was found to be more photocatalytically efficient than the sol–gel TiO₂ film prepared from the sol without the addition of PEG. Unlike the powdered samples calcined at 550 °C, Raman spectral analysis shows that TiO₂ films calcined at this temperature and used in photocatalytic experiments contains only anatase phase without conversion to rutile phase.

The removal of colour and the dye itself was more rapid and complete than the removal of TOC of the dye solution.

The kinetics of the photocatalytic degradation process of the Lissamine green B (LGB) dye dissolved in water follows the Langmuir–Hinshelwood model and depends on the properties (surface morphology) of prepared sol–gel TiO₂ films and the dye concentration.

Photodegradation of the LGB dye, carried out under UV-A radiation, indicated that the degradation was effective only in the presence of sol–gel TiO₂ films as photocatalysts. The influence of the photolysis and adsorption process on the removal of the dye from the solution is negligible.

Photocatalytic experiments were performed by the sol–gel TiO₂ films prepared from the sol without the addition of PEG.

4. Conclusions

On the basis of the obtained results, the following can be concluded:

- Nanostructured photocatalytic sol–gel TiO₂ films were successfully prepared without and with using PEG as a structure-directing agent.
- AFM study confirmed the nanocrystalline nature of the films prepared at 550 °C.
- The XRD patterns and Micro-Raman spectroscopy indicate the formation of crystallized mixed of anatase and rutile phases in powder samples prepared without and with the addition of PEG. Unlike the powdered samples calcined at 550 °C, Raman spectral analysis shows that TiO₂ films calcined at this temperature and used in photocatalytic experiments contains only anatase phase without conversion to rutile phase.
- The removal of colour and the dye itself was more rapid and complete than the removal of TOC of the dye solution.
- The kinetics of the photocatalytic degradation process of the Lissamine green B (LGB) dye dissolved in water follows the Langmuir–Hinshelwood model and depends on the properties (surface morphology) of prepared sol–gel TiO₂ films and the dye concentration.
- Photodegradation of the LGB dye, carried out under UV-A radiation, indicated that the degradation was effective only in the presence of sol–gel TiO₂ films as photocatalysts. The influence of the photolysis and adsorption process on the removal of the dye from the solution is negligible.
- The sol–gel TiO₂ film prepared from the sol with the addition of PEG was found to be more photocatalytically efficient than the sol–gel TiO₂ film prepared from the sol without the addition of PEG.
- Although this experimental set-up the decolourisation process was almost completed in 2 h, the total mineralization of the dye was not achieved. For total mineralization, the period of radiation exposure of the solution should be prolonged.

Acknowledgements

This study was supported by the Ministry of Science, Education and Sports of the Republic of Croatia within the framework of the Projects: 120-1253092-3021, 120-1201833-1789 and 098-0982934-2744.

References