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Screen-printing of TiO_2 photocatalytic layers on glazed ceramic tiles

P. São Marcos [a], J. Marto [a], T. Trindade [b], J.A. Labrincha [a,*]

[a] *Ceramics and Glass Engineering Department, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal*
[b] *Chemistry Department, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal*

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Abstract

In this work TiO_2 layers have been deposited by screen-printing in common glazed ceramic tiles. These TiO_2 layers were evaluated for the photocatalytic degradation of Orange II in aqueous solutions, in a batch photoreactor under visible light, and compared with TiO_2 (anatase) suspensions. The photocatalytic behaviour of the TiO_2 was evaluated by taking into account experimental variables which include (i) firing temperature of the TiO_2 printed layer; (ii) layer thickness; (iii) operation time. Optimal processed layers showed an interesting decolourisation performance (over 90% efficiency after 7–8 h). The maximum decolourisation rate, assuming an apparent first order reaction, is over 0.050 min^{-1} and is close to values reported in the literature for supported TiO_2 photocatalysis under UV irradiation. We anticipate that these new ceramic materials might be developed as an interesting alternative to TiO_2 suspensions, for example in photocatalytic applications excusing the removal of the particles at the end of the process.

Keywords: TiO_2; Screen-printed layers; Glazed ceramic substrates; Visible light photocatalysis

1. Introduction

In recent literature it has been suggested that the photodegradation of coloured organic pollutants on semiconductor surfaces can be a remediation process of waste waters [1–6]. Among the various semiconductors employed, TiO_2 has been recognized as a good photocatalyst for the degradation of several organic contaminants [7–11] due to its high photoreactivity, chemical stability and low toxicity. When illuminated with an appropriate light source, the photocatalyst generates electron/hole pairs with free electrons produced in the conduction band leaving positive holes in the valence band. UV radiation has been commonly used as a stimulating source, but visible light (artificial, solar or sunlight) was also tested by several authors [12–15]. The photogenerated electron/hole pairs are capable of initiating a series of chemical reactions at the TiO_2 surfaces, which involve adsorbed organic pollutants and surfacial water species that result in the decomposition of the organic compounds. The formation of relatively harmless end products represents another attractive feature of this process; carbon dioxide and water are the main final products, together with NO_x and HCl for organic compounds containing nitrogen and chlorine.

Most studies related to photodegradation reactions have been carried out using suspensions of powdered TiO_2 (usually Degussa P-25) in the polluted aqueous solutions. However, from a practical point of view, the use of catalyst suspensions in slurry photoreactors may constitute a limitation because of filtration problems linked to the small size of the TiO_2 particles that should be removed from the treated stream. In general, such separation processes are expensive in terms of time, reagents and manpower [16].

Therefore, several attempts have been made to immobilize the catalyst on rigid and inert supports and this is a very active topic of research on TiO_2 photocatalysis [17–22]. For example, Yeber et al. have reported the use of TiO_2 Degussa P-25 fixed on glass Raschig rings to decolourise and to increase the biodegradability of chlorinated cellulose effluents [23]. In the same publication, glass-impregnated ZnO was reported to discolour efficiently the effluent wastewaters within 120 min treatment with concomitant total organic carbon (TOC) reduction of ∼50%. Fernandéz et al. [24] tried several substrates to immobilize TiO_2 powders, including Raschig rings, glass and quartz (fused silica), and steel. Similar substrates or common polymeric sheets (e.g. polyethylene) were tried by other authors [25–28].

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[*] Corresponding author. Tel.: +351 234370250; fax: +351 234425300.
E-mail address: jal@ua.pt (J.A. Labrincha).

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In this paper we wish to describe an alternative process to produce supported TiO_2 for photocatalytic purposes. We describe the facile deposition of TiO_2 layers using a well-known process in the ceramic industry and which is based on the screen-printing of common ceramic glazed tiles. To the best of our knowledge this is the first report on the use of this technique for the fabrication of photocatalytic layers on common used ceramic tiles.

2. Experimental procedure

2.1. Preparation and characterization of TiO_2 layers on ceramic glazed tiles

Active layers of anatase (Kronos) were deposited on commercial glazed ceramic tiles (Revigrés, PT) by the well-established screen-printing technique. Powders were characterized by XRD (Rigaku Geigerflex D/max-Series diffractometer) and their particle size distribution was obtained by laser dispersion (Beckman Coulter LS 230). The TiO_2 powders have an average particle size of 0.29 μm and a specific surface area of $12.94\,cm^2/g$, as determined by BET (Micromeritics Gemini).

In order to deposit the photoactive layers, the TiO_2 powders were suspended (1:1 wt.%) in a proper organic media (NF 1281, CERANDRO) and the layers were printed through different sieved screens (55 and 136 μm) on common monoporosa glazed tiles. Deposited layers (25 and $50\,g/m^2$) were then fired at temperatures ranging from 300 to 1100 °C, and the changes on the microstructure and thickness with temperature and printing conditions were monitored by SEM and XRD. The scanning electron micrographs of fired layers were obtained on a Hitachi, SU 70 microscope working at 40 kV, fitted with an energy dispersive spectroscopy accessory (EDX Detector: Bruker AXS, Software: Quantax). To record the XRD diffractograms, typical incident angles of $0.5''$ were used.

2.2. Photocatalytic activity measurements

In order to evaluate the photoactivity of the screen-printed TiO_2 layers, the dye Orange II (Fluka AG, Buchs, Switzerland, disodium salt) was selected as the organic substrate for the catalytic experiments. Thus, Orange II aqueous solutions (20 mg/L) were prepared by dissolving the dye in distilled water and then adjusting the solution pH to 10 ± 0.5 by addition of aqueous NaOH (1 M).

The reactions were carried out in a cylindrical batch reactor (2 L) which contains five ceramic tiles, as schematically shown in Fig. 1. The correct dimensioning of the reactor limited the increase of the bath temperature (<10 °C) during visible light irradiation. A Philips ML-160 W lamp was used as the visible light source and the area ($0.034\,m^2$) of the TiO_2 layers in direct contact to the dye solution was kept constant. For sake of comparison, photolysis and dark experiments (i.e. in the absence of the catalyst and without light stimulation, respectively) were performed using similar experimental conditions. In order to predict the inertness degree of the substrate towards the active layer, catalysts-free glazed pieces were also tested. Finally, the photodegradation of Orange II dye by TiO_2 suspended particles (1 g/L) was evaluated and used as standard.

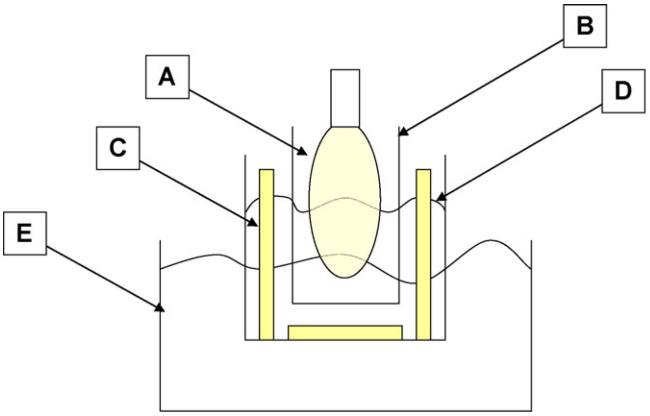

Fig. 1. Schematic view of the reactor set-up used during the photocatalytic experiments—A: lamp (Philips ML-160 W); B: glass protector; C: ceramic pieces containing screen-printed active layers; D: coloured solution reservoir (with stirring); E: cooling water reservoir (with stirring).

The photocatalytic activity of the materials was monitored by measuring the absorbance of collected samples of about 10 mL, after several running time intervals (up to 12 h). The UV–vis absorption spectra of the solutions were recorded with a Shimadzu UV-3100 spectrometer using water as the reference.

3. Results and discussion

3.1. Characterization of the substrates and screen-printed TiO_2 layers

The chemical composition of the glaze coating the ceramic tiles is given in Table 1; this coating is in direct contact with screen-printed TiO_2 layers and the data shown in Table 1 is typical for commonly used *monoporosa* glazes. Here, this type of glazed tile was chosen mainly because the TiO_2 content is null. In fact, in a control experiment, the photocatalysis of Orange II by the glazed pieces without screen-printed active layers was found to be ineffective. Similar findings on the unsuccessful degradation of Orange II and pheluric acid solutions using glazed ceramic pieces have been reported elsewhere [29].

Table 1
Chemical composition (XRF, Philips X'PERT PRO MPD) of a typical substrate monoporosa glaze that contacts with the screen-printed active layer (*detection limit)

Oxide	Wt.%
Fe_2O_3	0.13
TiO_2	<0.3*
CaO	11.1
K_2O	4.1
SiO_2	56.3
Al_2O_3	11.0
MgO	2.1
Na_2O	0.35
ZnO	7.5
ZrO_2	2.4
B_2O_3	3.8

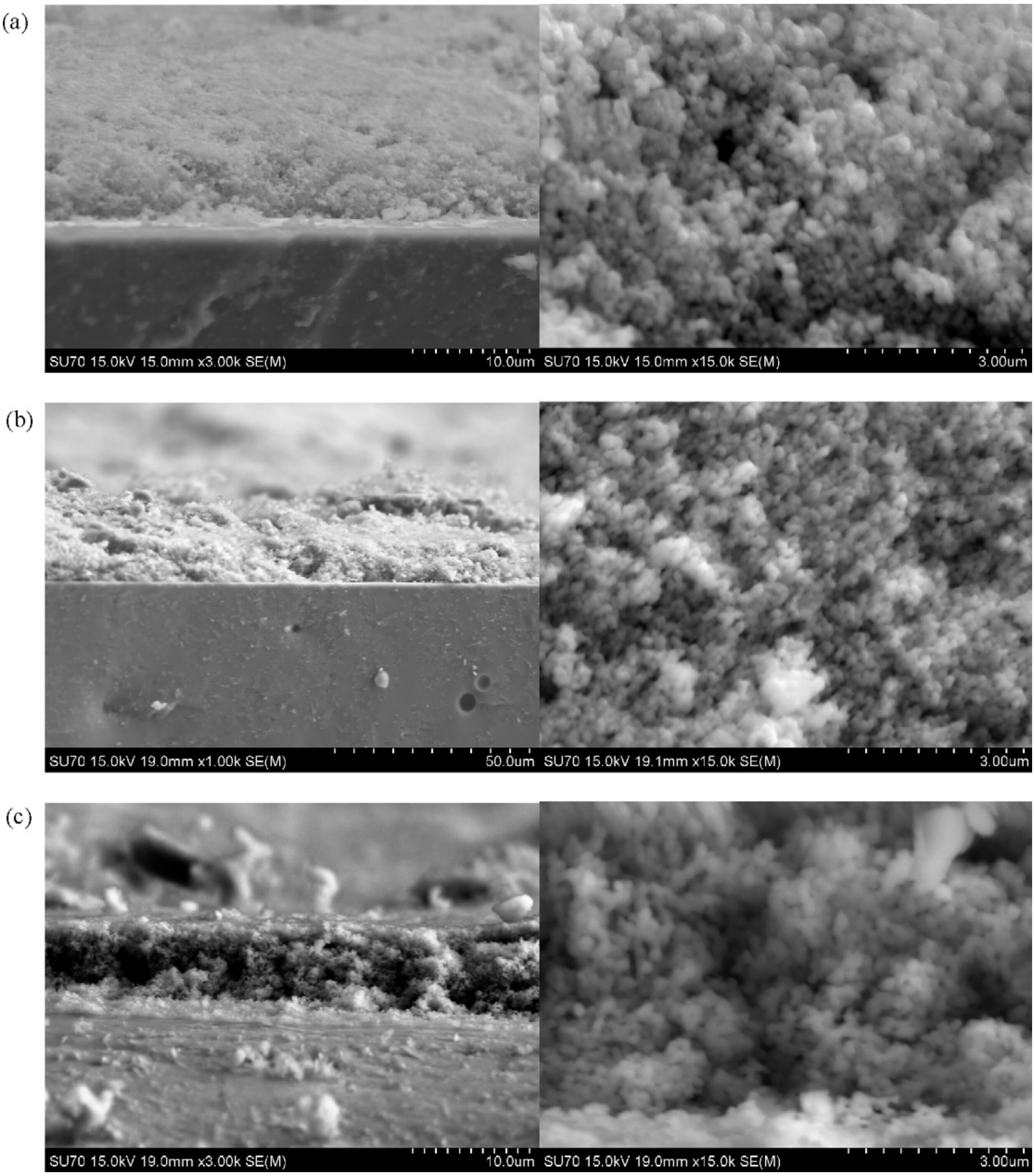

Fig. 2. SEM micrographs of TiO_2 screen-printed layers (25 g/m^2) fired at (a) 500 °C, (b) 600 °C, and (c) 950 °C.

Prior to the screen-printing deposition, the XRD of powdered TiO_2 was recorded confirming anatase as the only phase present. The typical texture and morphology of the TiO_2 screen-printed layers can be observed in Fig. 2, which shows SEM micrographs for samples fired at distinct temperatures. Instead of compact coatings, the TiO_2 layers appear with a granular morphology that in principle should be of interest for photocatalytic purposes due to their high-surface area. The SEM images of samples fired at temperatures up to 500 °C show some areas with a low microstructural definition, which might be due to the presence of organic vestiges coming from the medium used to suspend and print the active oxide. Particle size seems to not change significantly, denoting incipient sintering progression at least up to 950 °C but still the average particles size of TiO_2 remains well below 1 μm. Also the thickness of the screen-printed TiO_2 layers did not vary significantly for samples fired

Table 2
Layer thickness of deposited TiO_2 as estimated by SEM

Firing temperature (°C)/areal mass (g/m^2)	Thickness (μm)
500/25	5
500/50	10
600/25	8
600/50	7
850/25	5
850/50	12
950/25	6
950/50	17
1100/25	–[a]
1100/50	30

[a] The layer is indistinctive between catalyst and glaze.

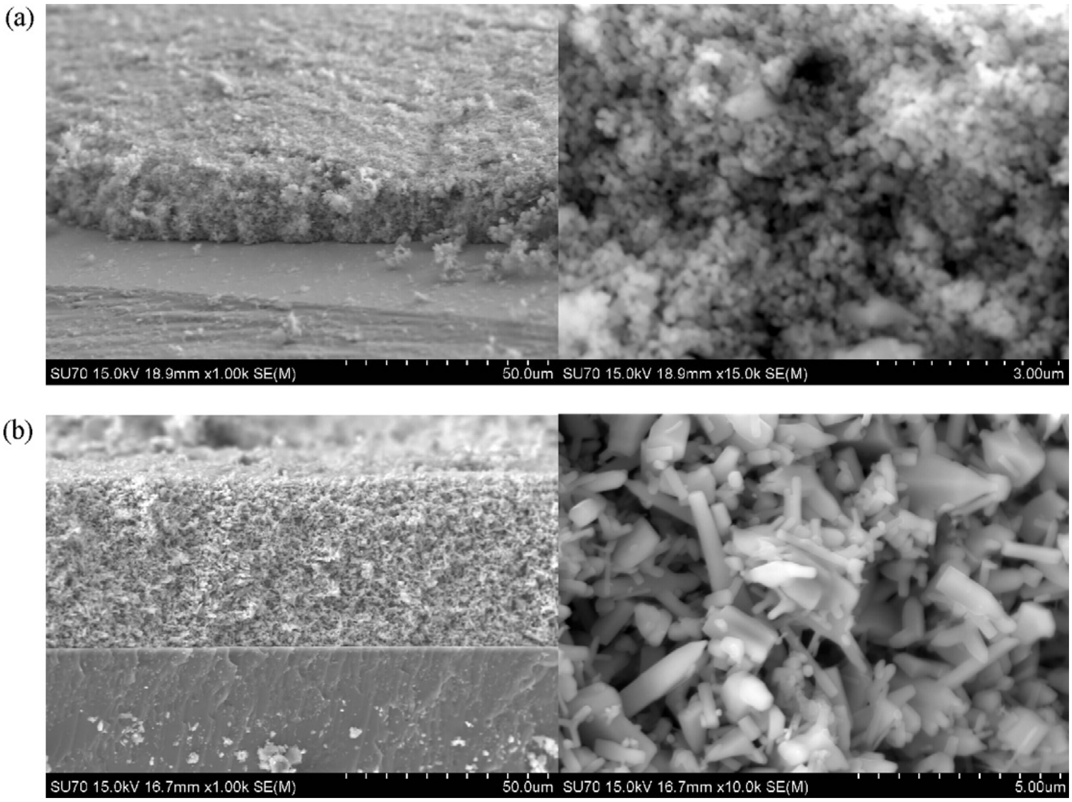

Fig. 3. SEM micrographs of printed TiO_2 layers (50 g/m^2) fired at 600 °C.

between 500 and 950 °C (Table 2). On the other hand, the layers thickness was largely affected by the deposition conditions, such as the use of a larger open sieved screen (136 μm) which obviously creates thicker deposits. This is clearly evident by comparing the SEM micrographs shown in Fig. 3 with those in Fig. 2.

Fig. 4 shows the XRD patterns for the supported titania samples which have been thermally treated at 600 and 1100 °C. Anatase and rutile were the crystalline phases observed, and the relative amount of rutile tends to increase with increasing firing temperatures. At 1100 °C, only rutile is detected. This polymorphic transformation and the excessive reactivity of the active layer towards the glaze tend to reduce their photoactivity.

To detect the presence of foreign (and unwanted) elements that might diffuse from the glazed substrate to the TiO_2 layers, EDX analysis was performed on all the samples. Thinner layers (25 g/m^2) fired at 1100 °C showed signs of Si at the top surface of the layer. However, thicker layers (50 g/m^2) fired at the same temperature still remain clearly separated from the substrate, as revealed by SEM and EDX elements distribution map of Fig. 5. In this case, the observed decrease in the catalytic performance is mainly due to the absence of anatase. The estimation of the thickness of thinner layers thermally treated at this temperature is also difficult because an indistinctive reaction zone appeared involving the catalyst and the glaze (Table 2). So, this analysis also helped to define the optimal firing temperature for the deposited TiO_2 layers on the ceramic glazed tiles, suggesting that the optimal working temperature range varies from 600 to 950 °C, as also later confirmed by the photocatalytic measurements.

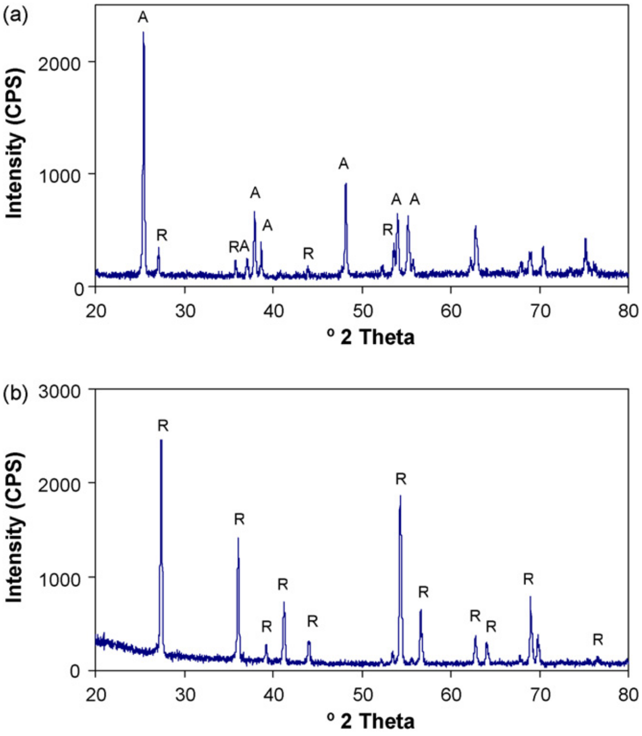

Fig. 4. XRD spectra of screen-printed TiO_2 layers (50 g/m^2) fired at (a) 600 and (b) 1100 °C (A = anatase; R = rutile).

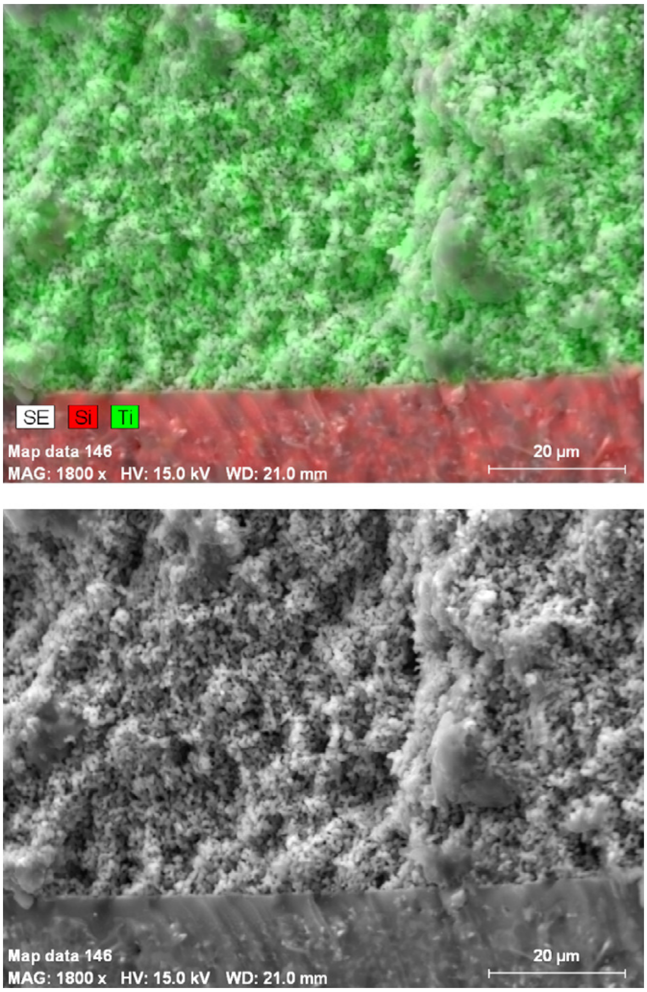

Fig. 5. SEM micrograph of printed TiO_2 layer (50 g/m^2) fired at 1100 °C (bottom); Ti and Si distribution maps, obtained by EDX upon an image generated by secondary electrons beam, are also given (on the top).

3.2. *Photocatalytic degradation of Orange II*

Prior to the photocatalytic degradation of Orange II in the presence of the screen-printed TiO_2 layers, control experiments in similar experimental conditions but without TiO_2 or in dark have been performed. Fig. 6 clearly shows that direct photolysis (without photocatalyst) of the dye is rather ineffective with a photodegradation degree less than 5%, after a reaction time of 7 h. By contrast, the adsorption of dye in the dark seems to have some significance, since absorbance at 486 nm tends to decrease more than 10% after 7 h (Fig. 7). We noticed that in this case the dye was mostly fixed in the backside of the ceramic pieces, i.e. in the surface uncovered by the glaze catalytic layer. In order to minimize this adsorption, the backside of the pieces was coated with an inert glue prior to their use in photodegradation experiments. By this way, attenuation of the 486 nm absorbance peak in the dark was kept below 5%.

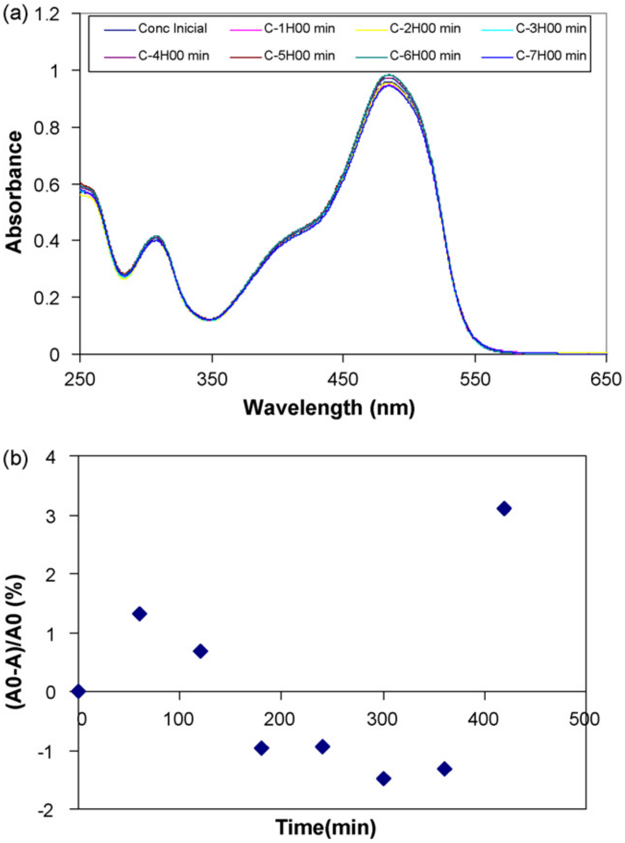

Fig. 6. Photolysis of Orange II dye performed in the batch reactor: (a) absorbance spectra; (b) attenuation (%) of the 486 nm absorbance peak.

Fig. 8 shows the kinetic curves representing the photocatalytic degradation of Orange II in contact with screen-printed TiO_2 layers which have been fired at 850 °C. A/A_0 gives the intensity attenuation of the characteristic band of the dye whose maximum is located at 486 nm. These results show that the screen-printed TiO_2 layers are effective in photodegrading Orange II, as denoted by the strong decrease of the peak height (more than 80% after 500 min testing). For comparison, the photodegradation results achieved by TiO_2 suspensions are given in Fig. 9. About 80% attenuation of Orange II absorbance peak was reached just within about 120 min. This was expected because as compared with the TiO_2 powders, the screen-printed TiO_2 layers (at 850 °C) have a lower surface area and also consist

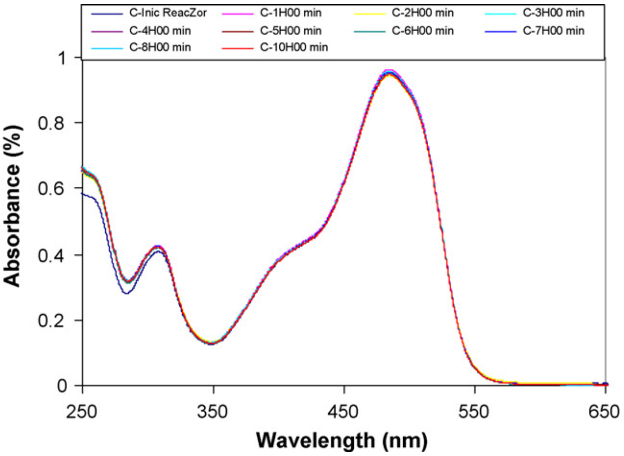

Fig. 7. Decolourisation of Orange II dye in the dark and just by contact with pieces having 50 g/m^2 screen-printed layers fired at 850 °C.

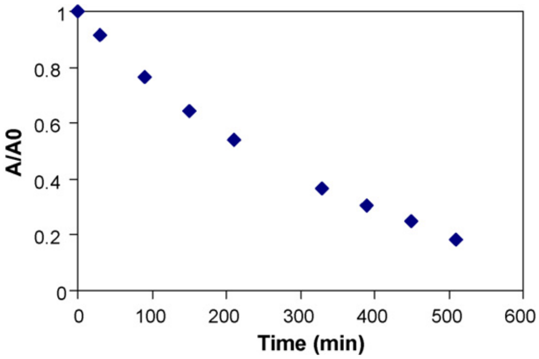

Fig. 8. Attenuation of the 486 nm absorbance peak of Orange II during photocatalysis with screen-printed TiO_2 layers (50 g/m^2) fired at 850 °C.

mainly of rutile, whose lower photoactivity has been reported when compared to its polymorph anatase [9].

A semi-quantitative analysis of the above results can be done by comparing the apparent rate constants of the photodegradation reactions, as suggested by Fernández et al. [24]. The photocatalytic degradation generally follows a Langmuir–Hinshelwood mechanism with the reaction rate being proportional to the photocatalytic material coverage (θ) with dye molecules.

$$r = k\theta = \frac{kKC}{1 + KC} \tag{1}$$

In Eq. (1), k is the true kinetic constant which includes parameters such as the mass of catalyst and the flux of efficient photons, C is the dye concentration in solution and K is the adsorption equilibrium constant. Since in the conditions of the experiment, the initial concentration of the dye is very low ($C_0 = 20$ ppm), the term KC in the denominator can be neglected with respect to unity and the rate law becomes, apparently, first order:

$$r = -\frac{dC}{dt} = kKC = k_a C \tag{2}$$

where k_a is the pseudo-first order kinetic constant. The integral form $C = f(t)$ of the rate equation is given by

$$\ln\left(\frac{C_0}{C}\right) = k_a t \tag{3}$$

Here we have measured the absorbance (A) of solutions containing the Orange II dye, which for each case is proportional to its concentration, thus similarly to Eq. (3) we can apply

$$\ln\left(\frac{A_0}{A}\right) = k_a t \tag{4}$$

The linear transforms $\ln A_0/A = k_a t$ of the curves in Fig. 8 are given in Fig. 10. In general a good correlation is obtained (>0.95, as shown in the inserted values of Fig. 10), suggesting that the reaction kinetics follows a pseudo-first order rate law. The slopes of the straight lines which all pass through the origin yield the apparent rate constants (k_a) that are given in Table 3. This table also show the maximum percentage decolourisation (A/A_0) and half-time values ($t^{1/2}$), corresponding to the time for which the dye is reduced to half of the initial amount.

These kinetic parameters suggest that the optimal firing temperature of the screen-printed TiO_2 layers is in the range 600–950 °C. From a technological point of view, this reasonably wide interval is very interesting since it means that some experimental tolerance is admissible to get optimal final results. However, the need to assure reproducible behaviour imposes operational constrains. Above 950 °C, there is evidence for reaction between the TiO_2 printed layers and the glazed support and the anatase polymorph almost disappeared, which might explain the detrimental effect on the catalytic behaviour of these materials. This effect is more pronounced when thinner TiO_2 layers (25 g/m^2) have been used. On the other hand, TiO_2 layers fired below 600 °C seem to show an incipient microstructural evolution, and organic vestiges related to the printing process were not totally removed, reducing the number of surface sites available for the catalytic process.

In general, thicker TiO_2 layers (50 g/m^2) were observed to show better photocatalytic degradation processes of Orange II under visible light irradiation (see Table 3). The amount of free active catalyst particles seems to be relevant in determining this effect.

The results above show that TiO_2 screen-printed layers on glazed ceramic tiles might be investigated as new materials for the photodegradation of organic pollutants. When compared with other results on catalysts supported on various substrates (glass, quartz, steel, polyethylene) [17–28], these results seem quite promising. For example, the reaction rate of Orange II decolouration by optimal TiO_2 layers ($k_a = 0.056$ min^{-1}) is comparable to the maximum values reported by Fernández et al. [24] on the degradation of malic acid by TiO_2 supported on glass,

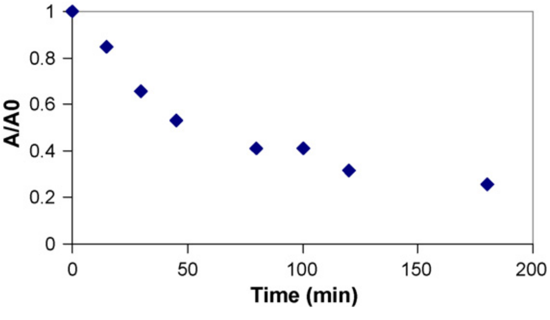

Fig. 9. Attenuation of the 486 nm absorbance peak of Orange II by suspended TiO_2.

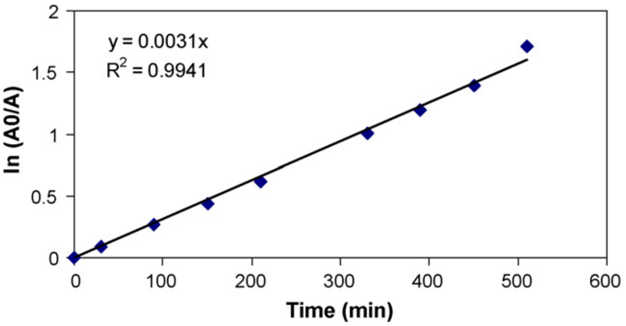

Fig. 10. Linear transforms $\ln A_0/A = f(t)$ of the kinetic curves shown in Fig. 8. Inserted values correspond to the slope (reaction rate, k_a) and correlation factor.

Table 3
Kinetic data for the Orange II photocatalytic decolourisation in contact with TiO_2 suspensions and TiO_2 screen-printed layers on glazed ceramic pieces: maximum decolourisation (%) and half-time ($t^{1/2}$) values are also given

Firing temperature (°C)/areal mass (g/m^2)	Rate constant (min^{-1})	Decolourisation (%)	Half-time (min)
500/25	0.022	82	325
500/50	0.041	95	202
600/25	0.029	91	279
600/50	0.035	85	210
850/25	0.019	59	360
850/50	0.040	93	195
950/25	0.013	42	569
950/50	0.056	89	126
1100/25	–	0	–
1100/50	–	0	–
Suspension	0.088	74	91

quartz and steel ($k_a \sim 0.069\,\text{min}^{-1}$). We should also remind that all the current experiments were conducted under visible light, while most reported values were obtained with UV irradiation.

4. Conclusions

In summary, TiO_2 layers have been deposited by screen-printing in common glazed ceramic tiles and proved to show interesting Orange II decolourisation performance (over 90% efficiency after 6–8 h) under artificial visible light. When compared with suspended TiO_2 powders, the kinetics is slower but overall acceptable decolouration levels were achieved in reasonable periods of time. However, it should be noted that the photocatalytic materials described here can be re-used, just after mere rinsing of the tiles in distilled water, and without affecting the photocatalytic activity. This indicates that the TiO_2 deposited layers are not de-actived during the reaction either by loss or poisoning of the catalyst, and can be re-utilized in subsequent runs. Moreover, screen-printing is a cheap and well-established technique in the ceramic industry to deposit glazes and decorations in ceramic tiles that also need second or third firing stages in running processing conditions, so it is predictably easy to implement with available technology. Besides water treatment processes, the photodegradation of aerial contaminants by ceramic facades containing such active layers is another interesting possibility. This is especially interesting because the chemical composition of the screen-printed material can be adjusted to specific working conditions, such as solar exposition levels and the nature of predominant pollutants. In this regards, the screen-printing of ZnO layers is at present under investigation in our laboratory.

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