Photocatalytic decolouration of Orange II by ZnO active layers screen-printed on ceramic tiles

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ABSTRACT

In this work ZnO layers have been deposited by screen-printing in common ceramic tiles. These layers were characterized and tested for the photocatalytic degradation of the organic dye Orange II in aqueous solutions, using a batch photoreactor either under visible light provided by a Philips ML-160 W lamp or under direct exposure to sunlight. For sake of comparison, ZnO suspensions have also been evaluated for similar reacting conditions. The influence of experimental parameters such as (i) firing temperature of the printed layer; (ii) layer thickness; and (iii) operation time have been investigated. Screen-printed ZnO layers obtained in optimal processing conditions showed photocatalytic activity comparable to aqueous ZnO suspensions. The maximal attenuation degree is over 70% and decolourisation rate, assuming that reaction kinetics follows a pseudo-first order rate law, is over $0.015 \, \text{min}^{-1}$.

Thus these ZnO-layered ceramic tiles can be regarded as an alternative to photocatalytic suspensions of the same material with the advantage of avoiding the removal of the photocatalyst.

1. Introduction

Recent studies have demonstrated that semiconductor heterogeneous photocatalysis can be employed to decompose organic dyes dissolved in water [1–4]. Due to their high photosensitivity, chemical stability and non-toxicity, TiO_2 and ZnO have been especially investigated in the degradation of several environmental pollutants [5–8]. When illuminated with an appropriate light source, these semiconductors generate electron/hole pairs, with electrons promoted to the conduction band and leaving positive holes in the valence band. The generated electron/hole pairs initiate a complex series of chemical reactions involving vestigial organic compounds adsorbed at the surface of the semiconductor that might result in the complete degradation of the adsorbates. Obviously, the formation of eco-friendly end products, as compared to the original pollutants, is an attractive feature of this process. Although UV light irradiation has been commonly in the photocatalytic studies involving ZnO ($E_g = 3.4 \, \text{eV}$), there has been a great interest in using visible light (artificial or sunlight) as the light source [9–12].

The use of ZnO catalyst slurries is reported in distinct works [13–17]. For example, Kansal et al. [13] tested the photocatalytic degradation of methyl orange dye, irradiating the aqueous solu-

tions of dye containing photocatalyst with UV and solar light and by changing several process parameters (amount of catalyst, concentration of dye, and pH). They found maximum decolouration (more than 90%) at basic pH (8–10) and under solar light irradiation. Daneshvar et al. [14] reported the removal of C.I. acid orange 7 from aqueous solution under UV irradiation in the presence of ZnO nanopowder and they stated that the complete removal of colour, after selecting desired operational parameters could be achieved in a relatively short time, about 60 min. In a different paper [15] some of these authors describe the photocatalytic degradation of acid red 14 dye by ZnO, again under UV irradiation. They concluded that degree of degradation of the dye is affected by illumination time, pH, and photocatalyst amount. The optimal amount of photocatalyst was 160 ppm, with dye concentration of 20 ppm. They also concluded that ZnO cannot be used in acidic solution. The complete removal of colour, after selection of optimal operational parameters, could be achieved in a relatively short time of about 1 h. The photocatalytic decolouration of azo-dye Orange II in water has been examined in an external UV light irradiation slurry photoreactor using ZnO by Nishio et al. [16]. They observed a two-stage decolouration process: the first stage of fast rate and the subsequent second stage where the rate is much slower. The efficiency of decolouration increased as initial dye concentration decreased and UV light intensity increased. There was optimal ZnO concentration around 1000 mg/L. The optimal pH was around 7.7, which was at the natural pH of the dye solution. Finally, Wang et al. [17] tested ZnO powders with various size scales (mean diameter size: 10, 50,

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200, and 1000 nm) prepared by two different preparation methods, thermal evaporation method and chemical deposition method, as photocatalysts for the UV-induced degradation of methyl orange in water solution. They concluded that preparation method was the decisive factor rather than size and morphology of powders.

As we may see, the vast majority of investigations in the area of photocatalytic degradation of pollutants have employed suspension of semiconducting particles. From a practical point of view, the use of catalytic slurries presents limitations related to the removal and leaching of the semiconductor particles. Usually this requires either long time sedimentation or centrifugation processes. Hence, there has been great interest in developing alternative strategies which include the coating of solid surfaces (e.g. glass, polythene, and cement) with photocatalytic layers [18–21].

Here we report photocatalytic studies involving the use of screen-printed ZnO layers on common ceramic glazed tiles, for distinct conditions of light irradiation. When necessary, the results obtained will be compared to those obtained in similar conditions for photocatalytic TiO$_2$ layers.

2. Experimental procedure

2.1. Preparation and characterisation of supported samples

Active layers of ZnO (Merck) were deposited on commercial glazed ceramic tiles (20 cm × 10 cm from Revigrés, PT) using a well-established screen-printing technique. The starting powders were previously characterized by XRD (Rigaku Geigerflex D/max-Series diffractometer) and their particle size distribution was obtained by laser dispersion (Beckman Coulter LS 230). The ZnO powders were 0.50 μm in average grain size of and showed a specific surface area of 1.56 m^2/g, as determined by BET (Micromeritics Gemini).

In order to deposit the photoactive layers, the ZnO powders were suspended (1:1 wt.%) in a organic medium (NF 1281, CERANDRO) and the layers were printed through distinct sieved screens (55 and 136 μm) on common bright monoporosa glaze tiles. The deposited layers (25 and 50 g/m^2) were then fired at temperatures ranging from 300 to 1100 °C. The influence of the temperature and printing conditions on the microstructure and thickness of the layers was monitored by SEM and XRD. The scanning electron micrographs of fired layers were obtained using 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 patterns of the deposited layers, typical incident angles of 0.5 in. were used.

2.2. Photocatalytic activity measurements

In order to evaluate the photoactivity of the screen-printed ZnO layers, the dye Orange II (Fluka AG, Buchs, Switzerland, di-sodium 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 the addition of aqueous NaOH (1 M).

The photocatalytic reactions were carried out in a cylindrical batch reactor (2 L), containing five ceramic tiles, as shown in Fig. 1. Any increase on the bath temperature due to light irradiation was limited up to 10 °C, due to the correct dimensioning of the photoreactor. A Philips ML-160 W lamp was used as the visible light source and the area (0.034 m^2) of the ZnO 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 irradiation, respectively) were performed using similar experimental conditions. In order to evaluate the influence of the
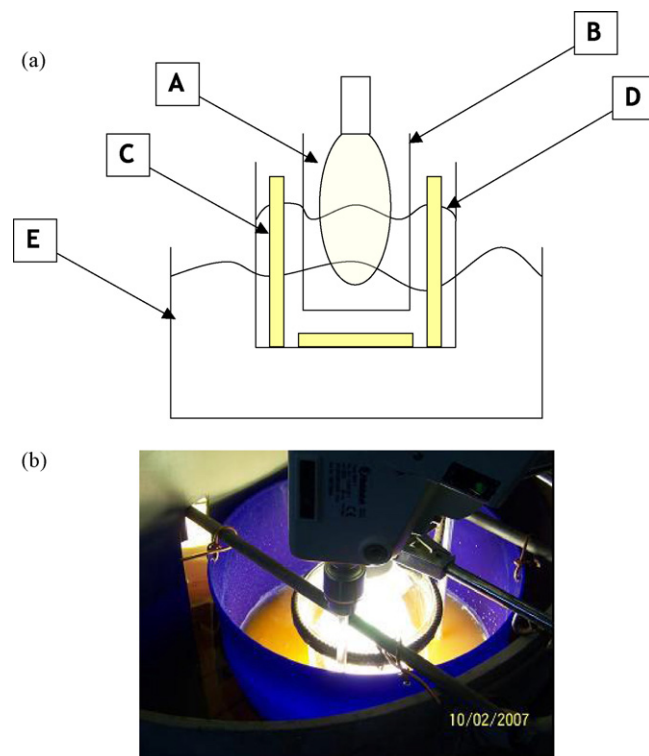

Fig. 1. (a) Schematic view of the reactor set-up used during the photocatalytic experiments: A, lamp (Philips ML-160 W); B, glass protector; C, ceramic pieces containing screen-printed active layers; D, coloured solution reservoir (with stirring); E, cooling water reservoir (with stirring). (b) View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

substrate towards the active layer, catalyst-free glazed pieces were also tested. The photodegradation of Orange II dye in the presence of ZnO suspensions (1 g/L) was used for comparative purposes.

The photocatalytic activity of all the materials was monitored by measuring the absorbance of the respective reacting solutions. As such, samples of about 10 mL have been collected for running time intervals (up to 12 h). The UV–vis absorption spectra were recorded using a Shimadzu UV-3100 spectrometer and using water as the reference.

3. Results and discussion

3.1. Characterisation of the substrates and screen-printed layers

Table 1 shows the chemical composition of the glaze that covers the ceramic piece contacting the screen-printed ZnO layers. This is a common bright monoporosa glaze and has been chosen for these studies due to its small ZnO content. In fact, our preliminary experiments for this work have shown that without ZnO screen-

Table 1
Chemical composition (XRF, Philips X'PERT PRO MPD) of the monoporosa glaze contacting the ZnO screen-printed active layer

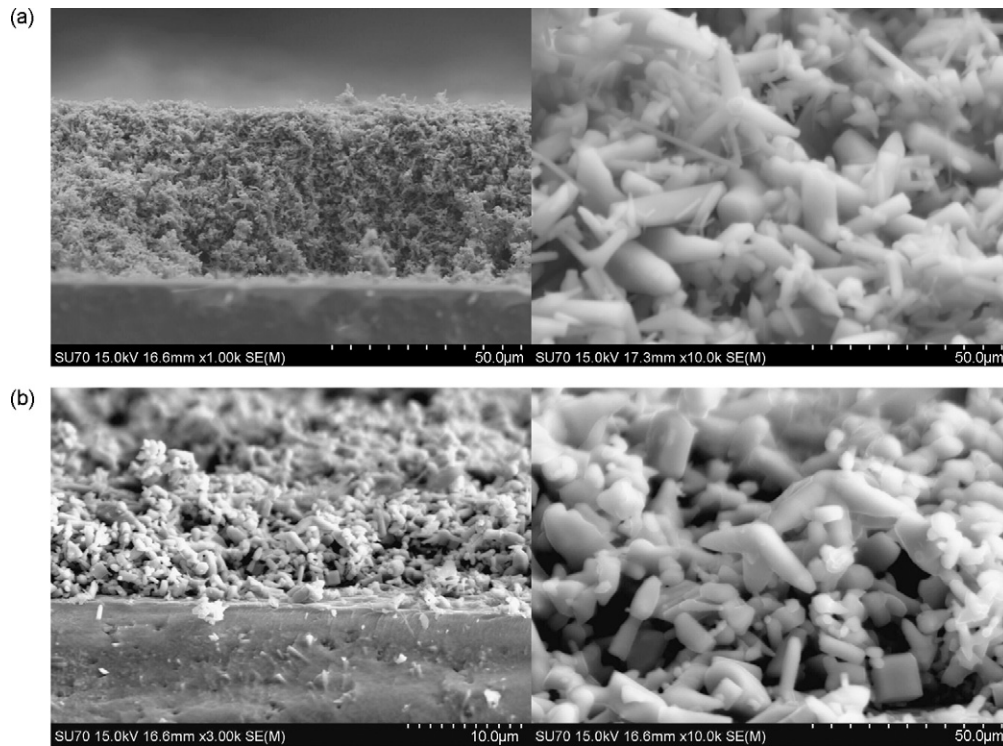| Oxide	wt.%
Fe$_2$O$_3$	5.4
TiO$_2$	1.0
CaO	0.1
K$_2$O	1.0
SiO$_2$	54.7
Al$_2$O$_3$	26.8
MgO	0.7
Na$_2$O	1.2
LoI	12.9

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

printed active layers, the glazes were ineffective concerning the photocatalytic degradation of Orange II. Similar findings have been reported for studies involving the photodegradation of Orange II and pheluric acid in the presence of glazed ceramic pieces [22].

Prior to the screen-printing deposition, the XRD of the starting ZnO powder was recorded confirming zincite as the only phase present. The SEM images (Fig. 2) of samples fired at distinct temperatures show the typical texture and morphology of ZnO screen-printed layers. Note that instead of compact coatings, the screen-printed layers appear with a granular morphology, which in principle should be of more interest for photocatalysis due to the higher 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 vestigial organic compounds from the medium used to suspend and print the active oxide. The average size of the ZnO particles varied between 1 and 3 μm. The layers thickness was mostly affected by the deposition conditions; the use of a larger open sieved screen (136 μm aperture) creating thicker deposits. This is particularly evident by compar-

ing the SEM micrographs shown in Fig. 3 with those in Fig. 2, for samples fired at the same temperature (please notice the distinct magnification of images on the left side).

The XRD of the deposited ZnO layers shows zincite as the single crystalline phase present without the formation of secondary phases, at least up to 950 °C (see Fig. 4). However, as will be discussed later, for temperatures superior to 1100 °C the reaction of the ZnO active layer towards the glaze tends to reduce its photoactivity. To detect the presence of foreign (and unwanted) elements that might diffuse from the glazed substrate to the ZnO layers, EDX analysis was performed in all the samples. For example, the samples fired at 1100 °C showed the presence of Si and Al in the top surface, as revealed by the elements distribution map shown in Fig. 5. Also for samples thermal treated at this temperature, the estimation of the layers thickness became very difficult because an indistinctive reaction zone appeared in between the ZnO catalytic layer and the glaze substrate (Table 2). Therefore the elemental analysis provides information that help to define an optimal firing temperature for the deposited ZnO layers on the ceramic glazed tiles. These results
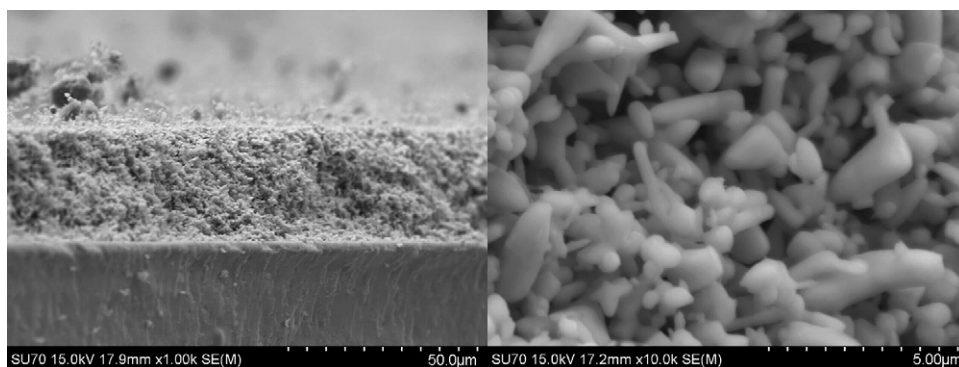

Fig. 3. SEM micrographs of printed ZnO layers (50 g/m^2) fired at 950 °C.
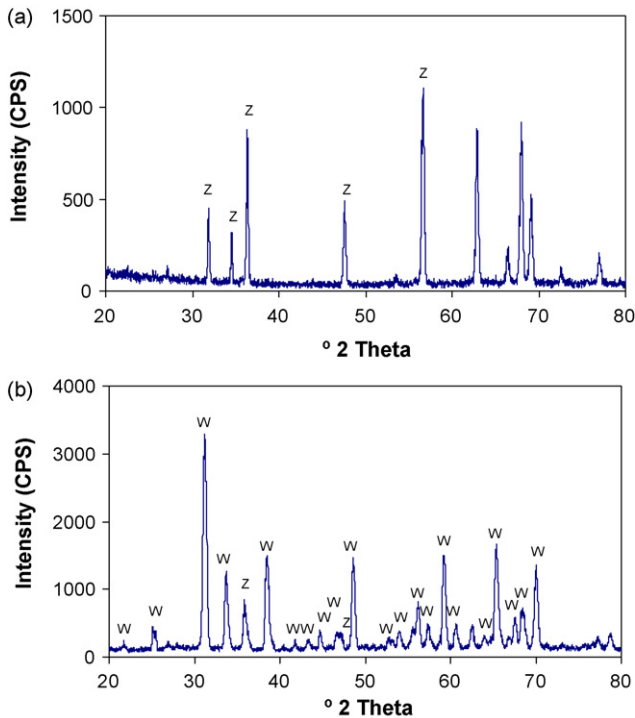
Fig. 4. XRD spectra of printed layers ($50\,g/m^2$) fired at 850 °C (a) and at 1100 °C (b). Z = ZnO; W = willemite (Zn_2SiO_4).

Table 2
Layers thickness of ZnO deposits, as estimated from SEM micrographs

Firing temperature (°C)/areal mass (g/m^2)	Thickness (μm)
500/25	5
500/50	36
600/25	5
600/50	41
850/25	5
850/50	35
950/25	6
950/50	29
1100/25	$-^a$
1100/50	35^a

The areal mass corresponds to the mass of active material (g) per unit area of the deposit.

^{a} The layer is a reactive zone between catalyst and glaze.

suggest that the window working interval varies from 600 to 950 °C, as will be later confirmed by the photocatalytic measurements.

3.2. Photocatalytic degradation of Orange II

Prior to the photocatalytic degradation of Orange II in the presence of the screen-printed ZnO layers, control experiments for similar experimental conditions but without ZnO (direct photolysis) or in dark conditions have been performed. Fig. 6 clearly shows that the direct photolysis of the dye is ineffective leading to a photodegradation degree less than 5%, after a reaction time of 7 h. Conversely, maintaining all the other experimental conditions, the dark experiments result in a decrease on the absorbance at 486 nm of more than 10%, suggesting that adsorption of the dye
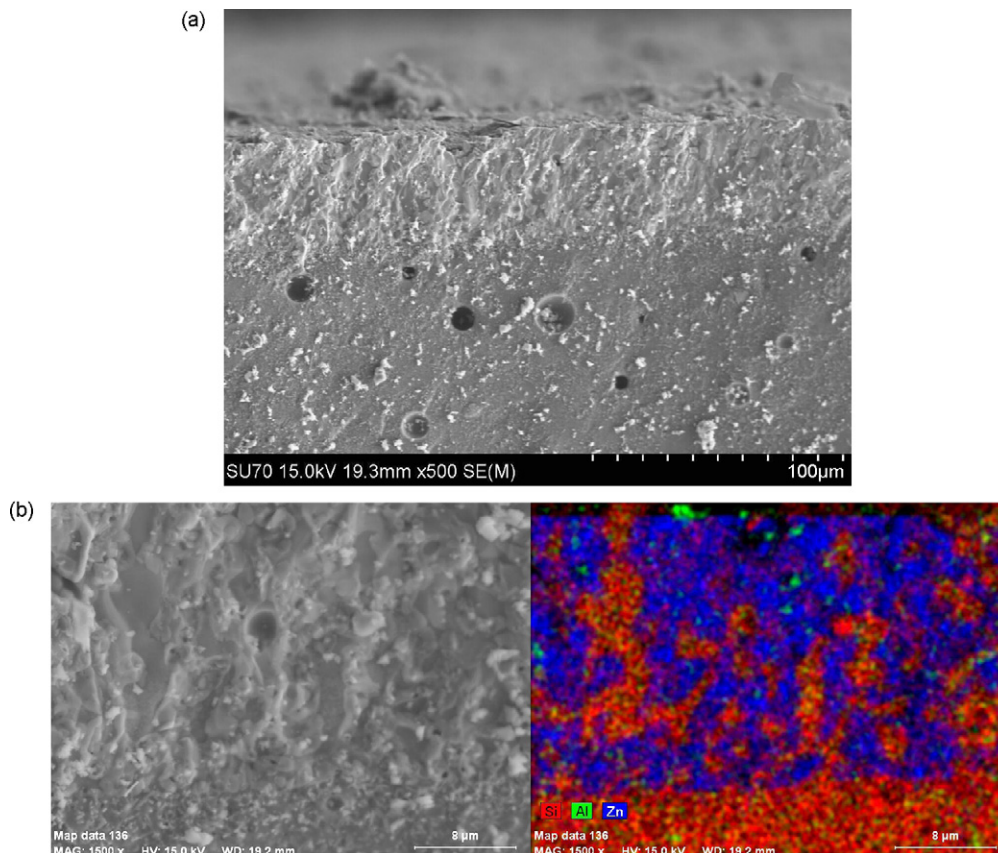

Fig. 5. (a) SEM micrograph of printed ZnO layer ($50\,g/m^2$) fired at 1100 °C; (b) Zn, Si, and Al distribution map, obtained by EDX upon an image generated by secondary electrons beam on the top surface. (For interpretation of the references to colour in this artwork, the reader is referred to the web version of the article.)
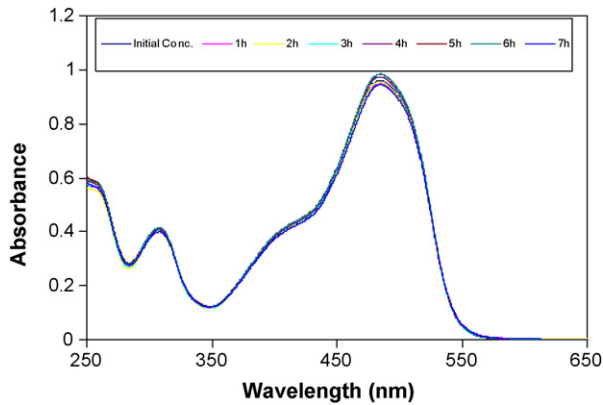
Fig. 6. Photolysis of Orange II dye performed in the batch reactor. (For interpretation of the references to colour in this artwork, the reader is referred to the web version of the article.)
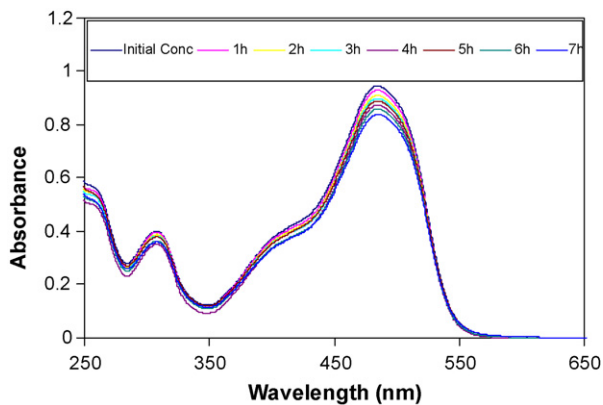

Fig. 7. Decolourisation of Orange II dye in dark conditions and when in contact with ZnO screen-printed ceramic pieces. (For interpretation of the references to colour in this artwork, the reader is referred to the web version of the article.)

at the tiles surfaces is relevant (Fig. 7). We have noticed that the dye was mostly adsorbed in the backside of the ceramic pieces, i.e. at the uncoated surface of the ceramic tiles. In order to minimize this effect, the backside of the tile was treated with inert glue prior to their use in the photodegradation trials. In this way, the decrease of the absorbance at 486 nm in dark conditions was kept below 5%.

Fig. 8 shows the kinetic curves representing the photocatalytic degradation of Orange II in contact with ZnO screen-printed layers ($50\,g/m^2$) that have been fired at $850\,°C$. The ratio A/A_0 gives the

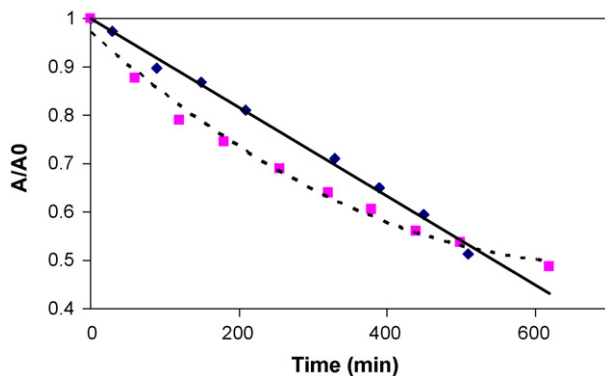**Fig. 8.** Attenuation of the typical absorption band of Orange II ($\lambda_{max} = 486\,nm$) during photocatalysis either in the presence of screen-printed ZnO layers ($50\,g/m^2$) fired at $850\,°C$ ($\blacklozenge$) or in the presence of ZnO suspensions ($\blacksquare$).

intensity attenuation of the characteristic band of the dye whose maximum is located at 486 nm ($\lambda_{max} = 486\,nm$). These results show that the screen-printed ZnO layers are reasonably effective in photodegrading Orange II, as denoted by the decrease of the band intensity ($\lambda_{max} = 486\,nm$) with running reaction time ($\sim$50% after 10 h). For comparison, results of the photodegradation of Orange II in the presence of ZnO suspensions are also shown in Fig. 8. For the earlier times of reaction, the use of ZnO suspensions result in higher attenuation degrees of the absorption band at $\lambda_{max} = 486\,nm$, as compared to the ZnO screen-printed layers, which is probably related to the higher surface area of the particulates. However, after about 10 h, a 50% attenuation degree of the absorption band ($\lambda_{max} = 486\,nm$) was observed which is comparable to the best performance achieved with the ZnO screen-printed layers. Moreover, the non-linear tendency observed using the suspended ZnO particles denotes a two-stage decolouration mechanism, as reported by Nishio et al. [16].

Following the methodology proposed by different authors [13,20], these results allow a semi-quantitative analysis by comparing the apparent rate constants of the photodegradation reactions. In these conditions, generally the photocatalytic reaction follows a Langmuir–Hinshelwood mechanism with the reaction rate being proportional to the photocatalytic material coverage (θ) with the 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 ($C_0 = 20\,ppm$), $KC \ll 1$ (Eq. (1)) and thus the rate law is 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

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

Since we have measured the absorbance (A) of solutions containing the Orange II dye, which for each case is directly proportional to the dye concentration, as 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. 9. In general a good correlation was obtained (>0.97, as shown in the inset of Fig. 9), suggesting that the reaction kinetics follows a pseudo-first order rate law. The slopes of the straight lines passing through the origin yield the apparent rate constants (k_a) depicted in Table 3. This table also gives the maximum 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 layers is in the range 500–950 °C. From a technological point of view, this relatively wide interval is interesting because it means that to get optimal results, there is some experimental tolerance concerning the materials preparation. However, the need to assure reproducible behaviour imposes operational constrains. Above 950 °C, there is evidence for reaction between the ZnO-printed layer and the glazed support (see Figs. 4 and 5) which might explain the detrimental effect on the catalytic behaviour of these materials. This effect is more pronounced when thinner ZnO layers ($25\,g/m^2$) were used. On the other hand,
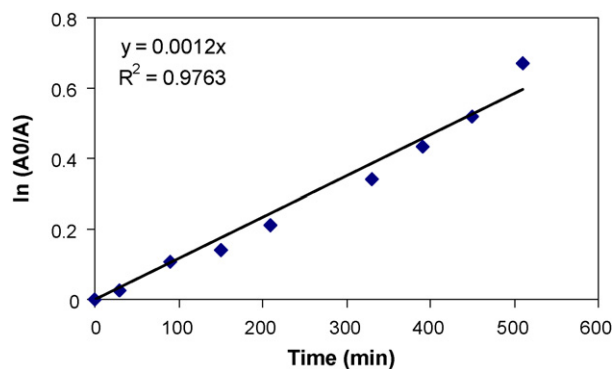
Fig. 9. Linear transforms $\ln A_0/A = f(t)$ of the kinetic curves shown in Fig. 7. Inserted values correspond to the slope (=reaction rate, k_a) and correlation factor.

ZnO layers which have been fired below 500 °C seem to shows 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.

The effect of the ZnO layer thickness in the photocatalytic degradation of Orange II under visible light irradiation seems to change with the firing temperature (see Table 3). At 500 °C, thinner ZnO layers (25 g/m^2) showed better performance than thicker ZnO layers, which is probably related to the presence of organic vestiges due to the printing process. By contrast, samples fired at 850 °C or above tend to show better performance when their thickness is higher. In fact, the amount of free and active ZnO particles is predictable to be higher in the thicker layers. In summary, among the samples evaluated in this study, the 50 g/m^2 ZnO layer fired at 850 °C showed the optimal performance.

At the moment, there are no reported data on the photocatalytic behaviour of ZnO supported layers, which preclude a direct comparison of our results with the literature data. However there are reported results for analogous TiO$_2$ materials. The reaction rate of Orange II decolouration by optimal ZnO layers ($k_a = 0.016 \, min^{-1}$) is somewhat lower than maximum values reported by Fernández et al. [20] on the degradation of malic acid by TiO$_2$ supported on glass, quartz, and steel ($k_a \sim 0.069 \, min^{-1}$). We should also remind that all the current experiments were conducted under visible light, while most reported values were obtained with UV irradiation. Kansal et al. [13] reported a rate constant of about $1.3 \times 10^{-3} \, min^{-1}$ in the decolouration of methyl orange dye (25 mg/L) under solar irradiation. Daneshvar et al. [15] estimated a rate constant of 0.0548 min^{-1} in the photocatalytic degradation of acid red 14 dye

Table 3
Rate constants for the photocatalytic degradation of Orange II using ZnO aqueous suspensions and ZnO screen-printed layers on glazed ceramic pieces

Firing temperature (°C)/areal mass (g/m^2)	Rate constant (min^{-1})	Decolourisation (%)	Half-time (h)
500/25	0.0008	47	14.4
500/50	0.0005	35	23.1
600/25	0.0010	45	11.6
600/50	0.0009	43	12.8
850/25	0.0006	29	19.2
850/50	0.0011	49	11.2
950/25	0.0007	25	16.5
950/50	0.0008	37	14.4
1100/25	–	0	–
1100/50	0.0007	27	16.5
Suspension	0.0013	51	9.8
Sunlight[a]	–	75	7.5

Maximum decolourisation (%) and half-time ($t^{1/2}$) values are also given.

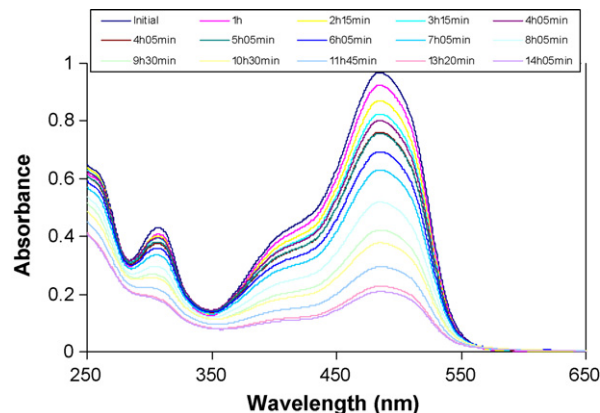[a] Test under sunlight was performed with 50 g/m^2 layers fired at 850 °C.

Fig. 10. Attenuation of the typical absorption band of Orange II ($\lambda_{max} = 486 \, nm$) during photocatalysis using screen-printed ZnO layers (50 g/m^2) fired at 850 °C, performed under direct exposure to sunlight. (For interpretation of the references to colour in this artwork, the reader is referred to the web version of the article.)

by ZnO suspension under UV irradiation. Nishio et al. [16] reported that the decolouration rate of azo-dye Orange II linearly depended on the UV-light intensity. The pseudo-first order reaction constant in the photoreactor with the impeller at 3.68 W m^{-2} could be estimated to be 0.0792 min^{-1}. We may then easily conclude that our estimation of the rate constant is not too far from those values.

Fig. 10 shows the spectra monitoring the photocatalytic degradation of Orange II in contact with ZnO screen-printed layers (50 g/m^2, fired at 850 °C) performed under direct exposure to the sunlight. Although in solar irradiation conditions the Orange II decolouration was still efficiently achieved with the ZnO layers, the fitting of the experimental data to a first order kinetics was not accurate and preclude a direct comparison with the tests performed in the photoreactor.

4. Conclusions

ZnO layers have been deposited by screen-printing in common glazed ceramic tiles and proved to show Orange II decolourisation performances (over 50% efficiency after 6–8 h, while maximum attenuation degree reached 72%), under artificial visible light or by direct exposure to the sunlight. Thus these coated ceramic tiles are promising materials for the photodegradation of organic pollutants under solar irradiation conditions. Compared to suspended ZnO powders, the kinetics is in fact slower but overall the decolouration levels achieved in reasonable periods of time were similar. On the other hand, it should be noted that the photocatalytic materials described here can be re-used just after mere rinsing of the tiles in distilled water without affecting the photocatalytic activity. This indicates that the ZnO deposited layers are not deactivated during the reaction either by loss or poisoning of the catalyst, and thus can be re-used in subsequent runs.

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