

DEVELOPMENT OF CERAMIC GLAZE WITH PHOTOCATALYTIC ACTIVITY: GLAZE WETTABILITY

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ABSTRACT

Glazes were developed by adding anatase to commercial ceramic frits as a photocatalysis agent. The glazes were coated on ceramic tiles, which were fired between 800 and 1000°C. The formulations were characterized (SEM, XRD), and the wettability was determined by measuring the water contact angle. The microstructural analysis (SEM) showed that the anatase particles can disperse properly in the glaze matrix. The X-ray diffraction shows that from 1000°C, the glaze becomes very reactive, and particles of anatase are transformed into titanite or rutile, depending on the glaze used. The determination of the contact angle shows the clear influence of the glaze type and sintering temperature on the wettability characteristics of the obtained layer.

1. INTRODUCTION

Photocatalytic semiconductors have attracted much attention because they are a low cost and non-toxic alternative to develop photoactive surfaces that could destroy organic compounds by oxidation reactions. In addition, the semiconductor particles can be immobilized in a thin layer on any surface, and can maintain their activity after repeated catalytic cycles (1). Among the various available semiconductors, such as metal oxides (e.g. TiO_2 , ZnO and CeO_2) and metal sulfides (e.g. ZnS or CdS), titania (TiO_2) has been the most suitable for photocatalysis and photovoltaic activity because of its relatively high quantum yield (2).

Titanium dioxide has two main catalytically active crystalline phases, anatase and rutile. The anatase form is generally more photoactive and is widely used in environmental applications, such as water purification, recycled water treatment and air purification (3, 4). Titanium dioxide is also known for properties such as chemical durability, thermal stability, high hardness, applications for white pigments and resistance to wear, being a material used for the development of protective coatings for ceramic tiles (5, 6). In fact, titanium dioxide is used as a self-cleaning coating on exterior surfaces, as it reduces and decomposes organic pollutants, removing dirt as grease and oil, thus allowing smaller maintenance costs or efforts (7, 8).

Currently there is a special interest in nanostructured materials due to their novel properties and functions related to their different electrical, mechanical, magnetic, optical, electronic and catalytic behaviour. Nanostructured titanium dioxide coatings are being developed with the aim of increasing hardness, toughness and mechanical strength as well as to provide resistance to corrosion and oxidation at high temperatures, with interesting antibacterial properties, besides their photocatalytic and photovoltaic properties (9-12).

Therefore, the aim of this research was the development of glazes for protecting and covering ceramic tiles for building facades. The ceramic tiles – tiles for building facades – firstly undergo a conventional manufacturing process and a special layer of glaze can, subsequently, be applied on their surfaces, giving them various properties that make them functional coatings. The process of using an already fired ceramic tile and the application and firing of a new layer (glaze) is currently used in the ceramic industry, a process called “third firing”, usually used for aesthetic purposes, such as the application of metallic surfaces.

Coatings with catalytic properties, i.e., which can be activated by UV radiation, can form surfaces with a number of special features, based on the ability of such coatings to interact with UV radiation, and also change the surface wettability and facilitate water runoff that is deposited naturally or artificially on these surfaces (13-15).

Due to their inorganic nature, coatings with catalytic properties are non-combustible and are resistant to conventional cleaning agents. As indicated, the

properties of these coatings are activated by UV radiation, which produces a series of internal changes in the electronic structure of the coating, but does not affect its appearance and the technical characteristics of its macroscopic surface (hardness, chemical resistance, etc.). UV radiation is present in daylight (even without direct sunlight) and partly in some artificial light sources. Therefore, this type of coating is particularly suitable for exterior and interior areas exposed to enough natural light, or with adequate artificial light sources. The activating effect generated on the surface does not disappear immediately when the radiation ceases, but lasts for a sufficiently long time (longer than the night period) to ensure their effectiveness (16-18).

In addition, some of these coatings significantly increase the contact angle between the workpiece surface and water, thereby favouring the formation of drops in which dust particles adhere. The drops easily slide on this surface, carrying the dirt and helping to keep the surface free of inert material (dust, dried vegetable debris, etc.). This effect provides photocatalytic coatings with another type of functionality, to keep surfaces clean, avoiding also the proliferation of microorganisms. The hydrophobic coatings used on glass surfaces consist of a combination of organic and inorganic materials with nanometric dimensions, which increase the surface tension, thus contributing to the properties of the surface on which they were applied. Other coatings exhibit the hydrophilic effect, where droplets of water deposited on them decrease their contact angle with the photocatalytic surface after exposure to UV radiation, forming a highly uniform thin film of water, which behaves optically like a clear sheet of glass, avoiding the fogging of the surfaces.

Therefore, the objective of this work was the development of photoactive glazes from commercial frits with the addition of TiO_2 in the anatase form, which were applied over already glazed ceramic tiles.

2. EXPERIMENTAL PROCEDURE

In this work two commercial ceramic frits (with low softening point), halite (NaCl) and commercial anatase were used. The frits were chemically (XRF and AAS for B element) and thermally (optical dilatometry, $40^\circ\text{C}/\text{min}$, air atmosphere) characterized. For anatase, the chemical composition (XRF), particle size (laser diffraction), and crystalline structure (XRD, Cu K_α ($\lambda = 1.5418 \text{ \AA}$), 40 kV and 30 mA, 2θ from 10 to 90° , 0.05° step and 1 s time) were determined.

The photoactive glaze formulations were prepared with a 3:7:10:80 ratio of TiO_2 , frit or halite, dispersant and water (all mass %) respectively, and the formulations were vigorously stirred for subsequent deposition on ceramic tiles. The suspensions were applied by spraying on already glazed stoneware tiles ($10 \text{ cm} \times 10 \text{ cm}$), and the tiles were fired between 800°C and 1000°C in a 1 h cycle in a laboratory muffle furnace. After firing, the tiles were characterized by scanning electron microscopy (SEM). The hydrophilic (or hydrophobic) effect of adding anatase to the

ceramic glaze was determined by measuring the water contact angle on the tile surface at different UV-irradiation times with a contact angle goniometer system.

The photocatalytic activity of the samples was determined by the variation of the methylene blue concentration in aqueous solution (5 vol. %) in contact with the coated samples under UV irradiation in comparison with an uncoated sample. Initially the samples were kept for 30 min in the dark to allow the MB solutions to be adsorbed onto the samples surface. The absorbance of the methylene blue solutions (8 mL) was determined in a UV-visible spectrometer at 664 nm wavelength using water as the reference with the sample solutions collected during time intervals (up to 15 h).

3. RESULTS AND DISCUSSION

The chemical analysis (XRF and AAS) of the frits is shown in Table 1. TEC frit is a borosilicate glass with sodium and zinc oxides; the loss on ignition is probably due to the presence of water. The SMT frit is made up of silica and calcium oxide with a small addition of borate and sodium and potassium oxides; the presence of a higher alumina content shows that this frit presents a higher softening point. Halite is a salt (NaCl, 99% purity).

Oxide (%)	SiO ₂	B ₂ O ₃	Na ₂ O	ZnO	Al ₂ O ₃	TiO ₂	K ₂ O	CaO	MgO	PPC
TEC	52.7	22.6	11.0	4.8	3.8	2.3	0.5	0.2	0.1	1.3
SMT	63.2	6.8	2.5	0.1	10.2	-	4.7	10.3	1.3	0.5

Table 1. Chemical analysis of the frits (XRF and AAS)

The thermal behaviour of the TEC and SMT frits and halite determined by optical dilatometry is shown in Table 2. The TEC frit is more adequate for a third-firing process than SMT due to its lower softening and melting temperatures as a result of its chemical composition. The SMT frit is more refractory than the TEC frit because of its higher content in alumina and silica and lower content in borate, besides the high content in calcium oxide. In turn, the halite shows intermediate behaviour between the TEC and SMT frits, with a small gap between the sintering and melting points, unsuitable for industrial use due to the great viscosity variation in a small temperature gradient. In addition, the release of Cl species during firing promotes the formation of HCl and subsequent corrosion of all machinery. Although widely used in the fabrication of industrial frits in Brazil, the use of halite is not appropriate in the ceramic industry.

Regarding the TiO₂ powder, the XRD analysis confirmed that it was mostly composed of anatase (90% by Rietveld analysis). The particle size distribution analysis shows that the anatase powder is submicron, what is not interesting for

promoting photocatalytic activity, since the photocatalytic activity is a function of the crystal phase and size. A nanocrystalline anatase phase would be preferred.

Temperature (°C)	Sintering	Softening	Sphere	Half-sphere	Melting
TEC	603	610	810	852	892
SMT	844	865	1105	1262	1315
HAL	786	787	-	-	812

Table 2. Thermal behaviour of TEC and SMT frits and halite (HAL) (optical dilatometry)

Figure 1 shows SEM images of the surfaces of the ceramic tiles after application of the anatase modified glazes and third-firing. At 800°C (a) the glaze composed of the TEC frit and anatase is partially stretched over the tile surface, covering the whole surface of the sample, resulting in some roughness. There are small particles on the surface. At 900°C (b) porosity and surface crystallization are present on the sample surface. Porosity is related to evaporation of some constituent of the glaze. The crystallization is due the effect of ZnO and anatase, it being noted that TiO₂ (anatase) had a strong effect as crystallization agent. Therefore, at 800°C there is formation of a glaze layer with proper texture. With respect to the glaze formed with halite and anatase, at both temperatures 800°C (c) and at 900°C (d) there was no homogeneous layer that could cover the entire surface of the tiles – the glaze apparently did not softened or stretch on the ceramic tiles surface, remaining only as a pre-glaze on the surface of the sintered samples. The glaze composed of the SMT frit and anatase even at 1000°C has not formed an even surface (not shown).

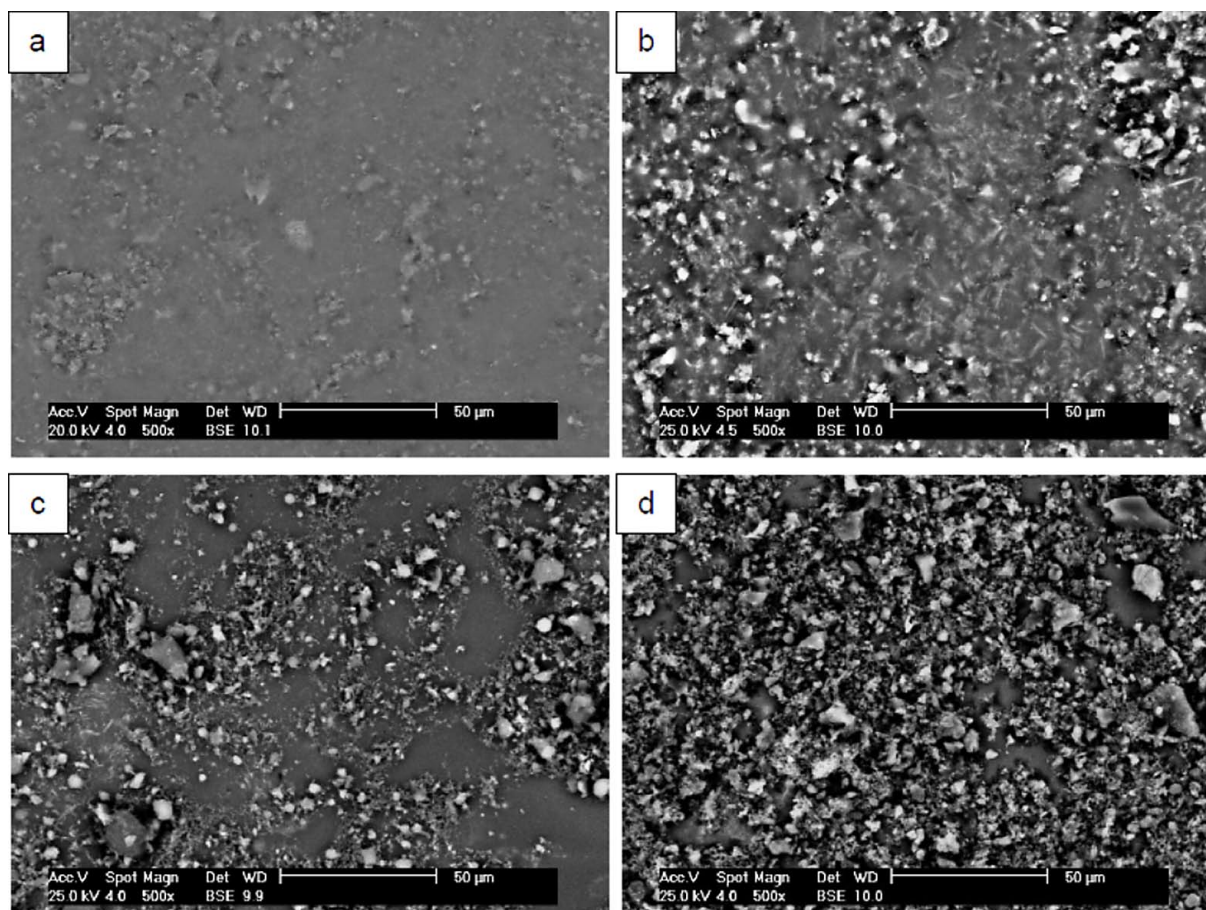


Figure 1. Surface of samples after third-firing: (a) TEC at 800°C, (b) TEC at 900°C, (c) HAL at 800°C, (d) HAL at 900°C (SEM)

The wettability test was used to determine the effect of the anatase addition on ceramic frits forming anatase-modified glazes on the surface of the tiles after third-firing. Photoactive tests are still on-going. Figure 2 shows the variation of the water contact angle depending on the type of frit used in the glaze and the firing temperature without UV irradiation. Without the modified glazes, the water contact angle with the original surface of the glazed tile is close to 10°. Without UV irradiation, the halite/anatase glaze fired up to 900°C shows a hydrophilic behaviour, with a water contact angle less than 10°. At 950°C firing temperature the glaze becomes more hydrophobic, with a water contact angle of 35°. Almost no substances show contact angles lower than 10° with the exception of some water-absorbing surfaces. Thin films composed of titanium oxide photocatalyst show hydrophilic behaviour only after exposure to UV light. The SMT/anatase glaze shows hydrophilic behaviour only at 800°C firing temperature and the TEC/anatase glaze do not show hydrophilic behaviour at any firing temperature. For all glazes, the increasing firing temperature promotes an increase of the water contact angle, without UV exposure.

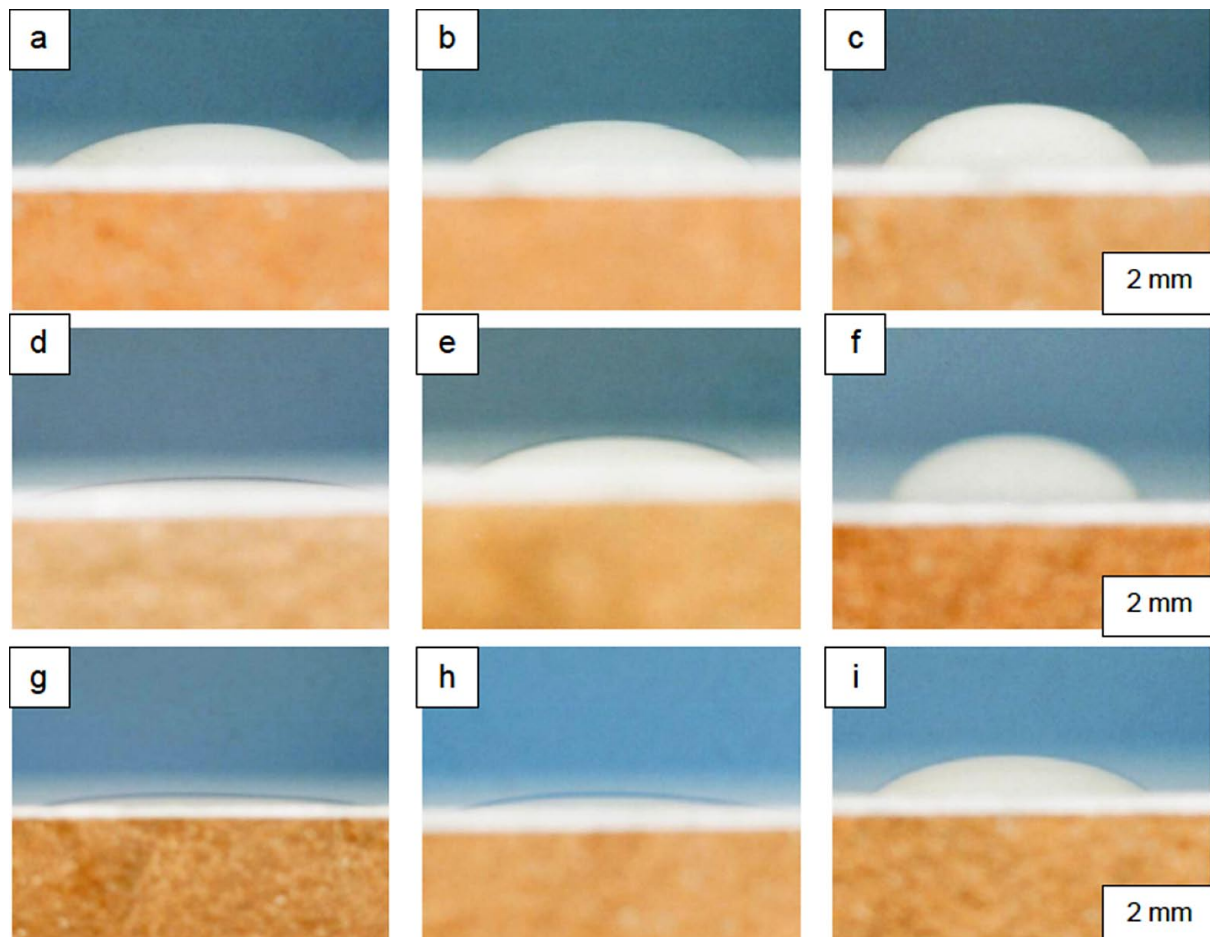


Figure 2. Contact angle for water depending on the type of frit and firing temperature: (a) TEC at 850°C, (b) TEC at 900°C, (c) TEC at 950°C, (d) SMT at 850°C, (e) SMT at 900°C, (f) SMT at 950°C, (g) HAL at 850°C (h) HAL at 900°C, (i) HAL at 950°C

Figure 3 shows the variation of the water contact angle depending on the type of frit used in the glaze and the firing temperature after UV irradiation. At zero time, without UV irradiation, there are some differences regarding the contact angle measured in Fig. 2, but the goniometer is a much more precise instrument than a digital camera. Once more, for all glazes, the increasing firing temperature promotes the increase of the water contact angle after UV exposure. With increasing UV exposure time the SMT/anatase and halite/anatase glazes show hydrophilic behaviour (contact angle $< 10^\circ$) for low firing temperatures, Figs. 3a and 3c. TEC/anatase glaze (Fig. 3b) shows marginal hydrophilic behaviour at low firing temperatures.

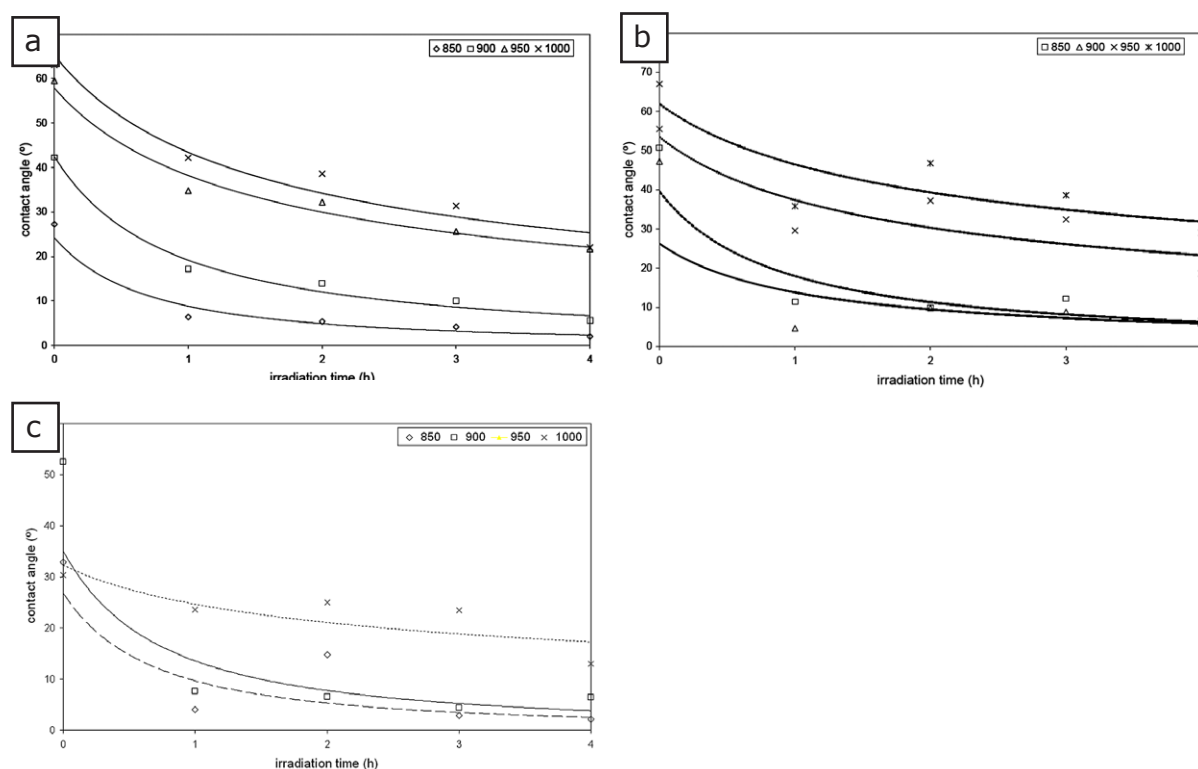


Figure 3. Contact angle for water depending on the type of frit and firing temperature after UV irradiation: (a) SMT/anatase glaze, (b) TEC/anatase glaze, (c) HAL/anatase glaze

There are two possibilities for the decrease in the water contact angle after long periods of UV irradiation: first, the samples present photocatalytic behaviour, and the mixing of anatase powder with low softening temperature frits was successful; or second, at low temperatures the glaze was not completely melted on the surface samples and after long periods of UV exposure the surfaces were cleaned and water was absorbed by the pores of the non-melted glaze.

The photocatalytic activity can be expressed as the rate of degradation of methylene blue in contact with the tile surfaces after UV irradiation during a period of time. The rate of degradation of methylene blue is expressed in terms of the residual concentration of MB as a function of time or the duration taken for the degradation of the pollutant (MB in this case). Fig. 4 shows the plot of $\ln(C_0/C)$ vs. irradiation time for SMT/anatase, TEC/anatase and halite/anatase glazes fired at 850°C and 900°C. The apparent rate constants for all glazes were very low, Table 3, showing that none of the glazes exhibit a real photocatalytic effect in comparison with a non-coated glazed tile.

Besides, some works (19-24) present ceramic tiles with photocatalytic properties processed with the same technique described here – coating of glazed tiles with a suspension of TiO_2 and frit and application by spraying or silk screen – the results obtained here were totally different. There was very little degradation of the methylene blue after five hours of exposure to UV light with a peak at 365 nm wavelength and intensity of 25 W/m². The rate of degradation of MB could even

be associated with the effect of photolysis during the experiments, explaining the poor fit of the curves (<0.99). The reasons for the residual photocatalytic behaviour of the frit/anatase doped glazes are: (1) the TiO_2 powder used does not present photocatalytic properties due its large particle size distribution (submicrometric); (2) the amount of TiO_2 used was very low (3 mass %) and TiO_2 particles were surrounded by the melted frits during third-firing, therefore not being exposed at the surface of the tiles; (3) the firing temperature was very high, because beginning at 800°C the anatase phase transforms to rutile phase, with lesser photocatalytic activity. Further studies are being conducted with different anatase/frit ratios and with a standard P25 anatase powder.

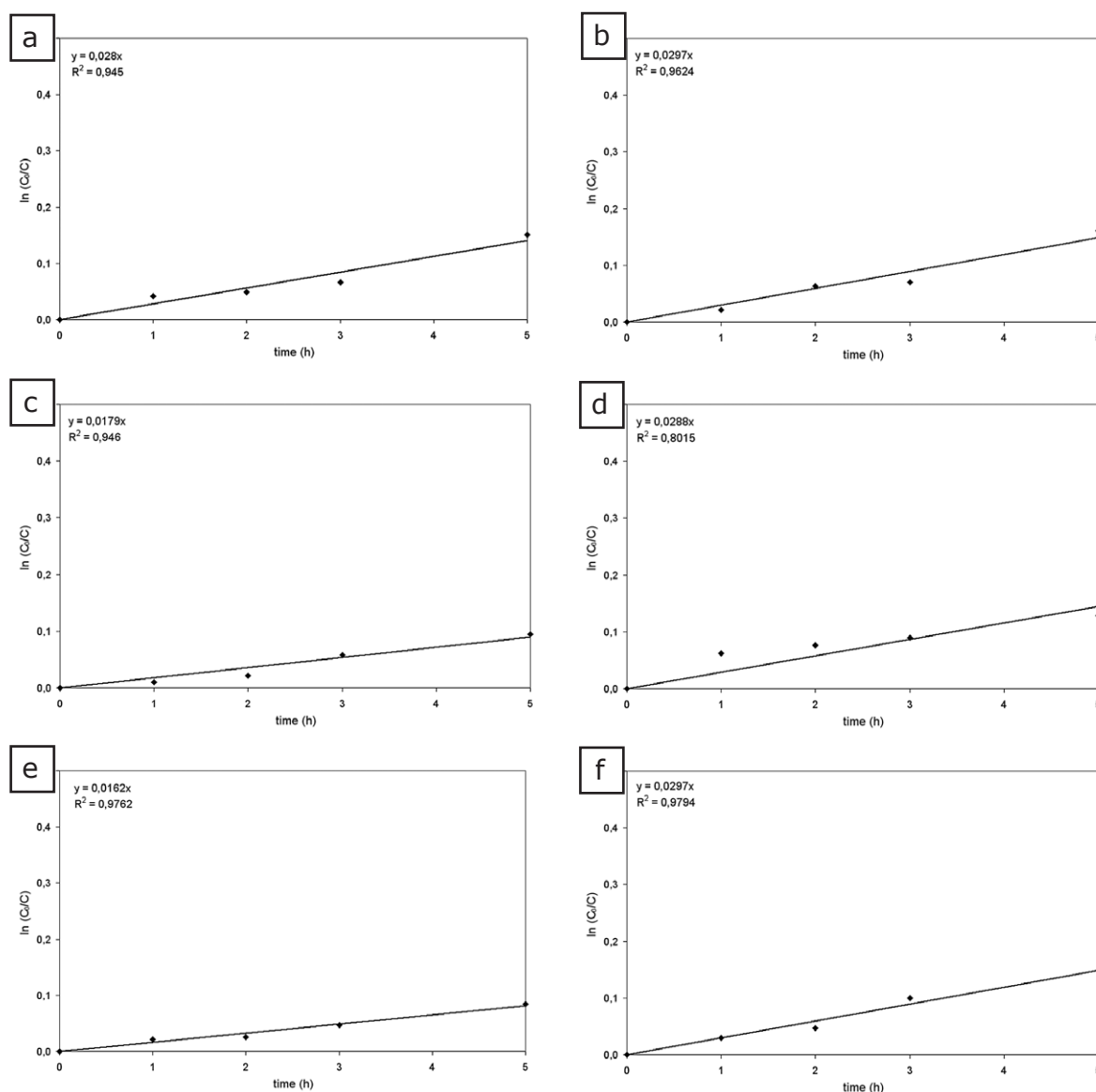


Figure 4. Plot of $\ln(C_0/C)$ vs. irradiation time for (a) SMT/anatase glaze fired at 850°C , (b) SMT/anatase glaze fired at 900°C , (c) TEC/anatase glaze fired at 850°C , (d) TEC/anatase fired glaze at 900°C , (e) halite/anatase glaze fired at 850°C and (f) halite/anatase glaze fired at 900°C

Sample	Rate of degradation (%)	Apparent rate constant (h ⁻¹)
Non-coated tile	8.3	0.011
SMT/anatase fired at 850°C	14.0	0.028
SMT/anatase fired at 900°C	14.8	0.030
TEC/anatase fired at 850°C	9.0	0.018
TEC/anatase fired at 900°C	12.0	0.029
halite/anatase fired at 850°C	9.1	0.016
halite/anatase fired at 900°C	13.7	0.030

Table 3. Rate of degradation (%) and apparent rate constant (h⁻¹) for the frit/anatase glazes fired at 850 and 900°C (after 5 h UV irradiation)

4. CONCLUSION

Ceramic glazes were prepared with a submicron anatase powder and low melting temperature frits. The glazes were applied on stoneware tiles and fired between 800 and 1000°C and the fired samples were tested for photocatalytic activity and hydrophilic behaviour. The main results are:

1. After firing the anatase powder seems to be very well dispersed in the glaze matrix;
2. The SMT/anatase and halite/anatase glazes display hydrophilic behaviour (contact angle < 10°) at low firing temperatures after UV irradiation;
3. None of the glazes (frit/anatase) have shown expressive photocatalytic activity.

The apparent hydrophilic behaviour may be explained by the porosity of the glazes at low firing temperatures, as the long irradiation time probably leads to cleaning of the tile surface and promotion of water absorption. Also, the low photocatalytic activity may be explained by the anatase powder particle size (submicrometric and not nanometric) or an excess of glaze that covers the anatase particles and prevents their surface activity.

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