Micro-sized TiO_2 as photoactive catalyst coated on industrial porcelain grès tiles in water drug photodegradation

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Abstract
Pharmaceutical compounds and their metabolites raise worrying questions because they are continuously released and are not efficiently removed by conventional wastewater treatments; therefore, they are detected in groundwater, surface water and drinking water in increasing concentrations. Paracetamol and aspirin are two of the most common drugs employed as fewer reducer, analgesic and antinflammatory: they and their metabolites are very often found in river water, so their degradation is necessary in order to obtain water suitable for human consumption.
The present work is focused on the comparison of the photocatalytic performance of industrial active grés porcelain tiles covered with a commercial micro-sized TiO2 by industrial process using either conventional spray deposition and innovative digital printing methods. The photodegradation of two common and widely used drugs, namely aspirin and paracetamol, was investigated both individually and as a mixture, in both deionized and tap water. Aspirin and paracetamol possess di-substituted aromatic ring in ortho and para position, respectively, and these affect the mechanism pathway, the side reactions and the photodegradation/mineralization trends.
The experimental conditions were thus selected in order to investigate either the effects of the nature of pharmaceutical compounds when they were studied individually or in mixture and the role of the water medium, comparing distilled and tap water. In fact, the presence in water of both cations (Na+, Ca2+, etc) and anions, i.e. sulphates, nitrates, and/or bi/carbonates, may influence the different steps of the photocatalytic process modifying both the speed and the eventual deactivation of the surface photocatalytic coating.

Keywords
Digital printing deposition; Pharmaceutical compounds; Photactive tile; Titanium dioxide; water remediation

INTRODUCTION

Nowadays, thanks new analytical methods and procedures, we are aware that the water bodies need urgent actions to correct the adverse human impact and thus restoring the pristine environmental conditions. Directive (EU) 2013/39/EU and subsequent Directive (EU) 2015/1787 state new regulations to monitor the quality of the aquatic environmental with special attention for water devoted to human consumption (Official Journal of European Union 2016). Pharmaceutical compounds and their metabolites raise worrying questions because they are continuously released and are not efficiently removed by conventional wastewater treatments; therefore, they are detected in groundwater, surface water and drinking water in increasing concentrations (Rivera-Utrilla *et al.* 2013; Verlicchi *et al.* 2015). Advanced oxidation processes (AOP) allow to remove these recalcitrant organic compounds, thanks to the generation of free radicals (HO^-, O_2^-), with high reactivity and low selectivity (Dey 2009). TiO_2 catalyst powder has attracted considerable attention due to its biological and chemical stability, low cost and mainly its capability to exploit natural and renewable solar UV light to degrade at complete mineralization the organic pollutants (Linsebligher *et al.* 1995; Diebold *et al.* 2010). Its industrial applications are not practicable because of the difficult recycling of the ultrafine TiO_2 particles from the treated water (Kinsinger *et al.* 2015; Westerhoff *et al.* 2011) and therefore actually it is classified as emerging contaminants due to its adverse environmental/health impacts (Love *et al.* 2014). An alternative possibility is the employment of immobilized TiO_2 catalyst powder on suitable and effective support materials placed on the wall of the reactor or around the light source, in order to apply continuous industrial processes. The nature of the materials, inorganic (i.e. glass, metal, carbon, ceramic, zeolite) and organic (i.e. polymer and textile) are also investigated to assess the effectiveness of the active coating and therefore the resulting photodegradation behavior (Yao *et al* 2009; Zhaoa *et al.* 2012; Fateh *et al.* 2013; Bianchi *et al*. 2015).

New techniques have to be developed to prepare stable and re-usable catalysts minimizing the reduction of surface area that always occurs when changing from the slurry catalyst to coated surfaces. One recent progress is the digital printing technology, initially performed in several fields thanks to its great flexibility, low cost, high reproducibility of the resulting layers: small single droplets are ejected from the nozzles by short pressure pulse controlled via a computer program (Hutchings *et al.,* 2013*).*

Ceramic is a versatile material extensively applied to building industry, as walls, roofs, tiles and floors that can be considered a ready and viable choice in environmental application (Güngor *et al.* 2016). Industrial photocatalytic ceramic manufacturing was developed exploiting this technique and obtaining well-dispersed TiO_2 coating covering the supports with an excellent photocatalytic efficiency (Rawlings *et al*. 2006).

The present work is focused on the comparison of the photocatalytic performance of industrial active grés porcelain tiles covered with a commercial micro-sized TiO_2 by industrial process using either conventional spray deposition (patent n. WO2010146410) and innovative digital printing methods. The photodegradation of two common and widely used drugs, namely aspirin and paracetamol, was investigated both individually and as a mixture, in both deionized and tap water. Aspirin and paracetamol possess di-substituted aromatic ring in ortho and para position, respectively, and these affect the mechanism pathway, the side reactions and the photodegradation/mineralization trends (Amalric *et al.* 1996; Rincón *et al*. 2001; Karthika *et al* 2011).

The experimental conditions were thus selected to investigate either the effects of the nature of pharmaceutical compounds when they were studied individually or in mixture and the role of the water medium comparing distilled and tap water. In fact, the presence in water of both cations (Na^+, Ca^{2+}, etc) and anions, i.e. sulphates, nitrates, bi/carbonates, may influence the different steps of the photocatalytic process modifying both the speed and the eventual deactivation of the surface photocatalytic coating (Muhamad *et al.* 2010; Orellana-García *et al.* 2015; Rioja *et al.* 2016;).

EXPERIMENTAL SECTION

Materials and reagents

Porcelain grés tiles (GranitiFiandre SpA) were industrially manufactured through milling, blending and drying processes under high pressure with quartz, feldspar and then calcined at 1200 °C in kiln. Control tests were carried out to verify the porosity, the frost resistance, the water-proofing, the durability and the hardness of the material. Then the surface was covered with a mixture of micro-sized TiO_2 and SiO_2-based compounds by means of spray method deposition (Bianchi *et al.* 2013) or by a digital printing equipment with an appropriate tailored-ink. In both cases, the coated tile is then heated once more at 680 °C for 80 min in order to stabilize the glazed photoactive coating and permanently stick the TiO_2 micro-sized particles. A final brushing in wet condition is performed to remove the TiO_2 particles not perfectly attached to the surface.

The photoactive particles distribution at the ceramic tiles surface was characterized by SEM analysis at increasing magnification using a LEO 1430 scanning electron microscope (chamber pressure at 10^{-6} Torr and 20 keV accelerating voltage).

Aspirin (A) and Paracetamol (P) were supplied by Sigma-Aldrich at high-purity analytical grade and used without further purification. Their chemical features are listed in Table 1.

Deionized water was produced by a Milli-Q- water (Millipore) and the tap water was collected from the municipal water main; its chemical composition and chemico-phisycal characteristics (table2) were checked and compared to the analysis provided by the Municipal Laboratory of City Milan (Metropolitana milanese 2016).

Table 1. Molecular structures of aspirin and paracetamol

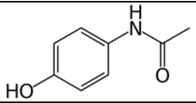
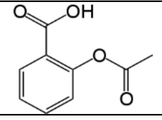
Nomenclature	Structure	Molecular formula
Paracetamol, Acetaminophen		$C_8H_9NO_2$
Aspirin, Acetylsalicylic Acid		$C_9H_8O_4$

Table 2. Tap water composition (mg L^{-1}) and chemico-phisycal characteristics.

$[F^-]$	<0.50	$[Ca^{2+}]$	86
$[Cl^-]$	34	$[Mg^{2+}]$	19
$[SO_4^{2-}]$	58	$[Na^+]$	18
$[NO_3^-]$	30	$[K^+]$	2
$[NO_2^-]$	<0.2	$[NH_4^+]$	<0.1
$[HCO_3^-]$	222	$[Mn^{2+}]$	<0.001
pH		7.7	
Hardness		31 °f	
Specific Conductance		681 μScm^{-1} (a)	

(a) at 20 °C

Photocatalytic Experiments

Photocatalytic degradations of pharmaceutical compounds were conducted in a batch reactor with 0.5 L volume. The temperature was fixed at 291 K using a thermostatic system and the agitation of polluted water was performed by a magnetic stirrer. Photon source was provided by a typical germicidal 9W UV-C lamp (Jelosil), characterized by a small UV-A radiation (0.5 W/m^2), directly immersed in polluted water in front of the photoactive tiles surfaces, as already reported in previous work (Bianchi *et al.* 2014)

A warm up time of 20 min was allowed to ensure consistent light output before irradiating the suspension. The tests were carried out at natural pH, namely 6.5 for deionized water and 7.7 for tap water.

The starting concentration of the drugs was fixed at 25 ppm in all test; therefore, the binary mixture of them was composed by 12.5 ppm of each pollutant. Every 60 minutes for the next 8 hours, and then at the end of the test at 24 hours, 2 ml of solution was withdrawn and analysed.

HPLC analyses were performed using Agilent 1100 Series Instrument, a diode array and with a 125 mm × 4 mm C18 reverse-phase column to follow the pharmaceutical compounds degradation. The mobile phase composition was methanol and water at 25:75 a volume ratio. The mineralization percentage was determined through the Total Organic Carbon (TOC) content. TOC was measured with a 5000 A Shimadzu.

RESULTS AND DISCUSSION

Fig.1 reports some SEM images relative to the two kinds of tiles prepared by spray deposition (left-hand sections) and digital printing (right-hand sections): the lower magnification images are useful to investigate the dispersion of the catalytic powder at the surface of the tile, whereas at higher magnification it is possible to inspect in detail the morphology of the coatings. The spray deposition surface is characterized by large agglomerates distinguishable only at higher magnification (see Figure 1c, left-hand image) and immersed in a glazed surface. On the contrary, the digital printing surface exhibits a well-dispersed coating also at lower magnification (see Figure 1a, right-hand image), then focusing on the TiO_2 particles it is possible to detect a covering layer composed by fine agglomerates (see Figure 1c, right-hand image).

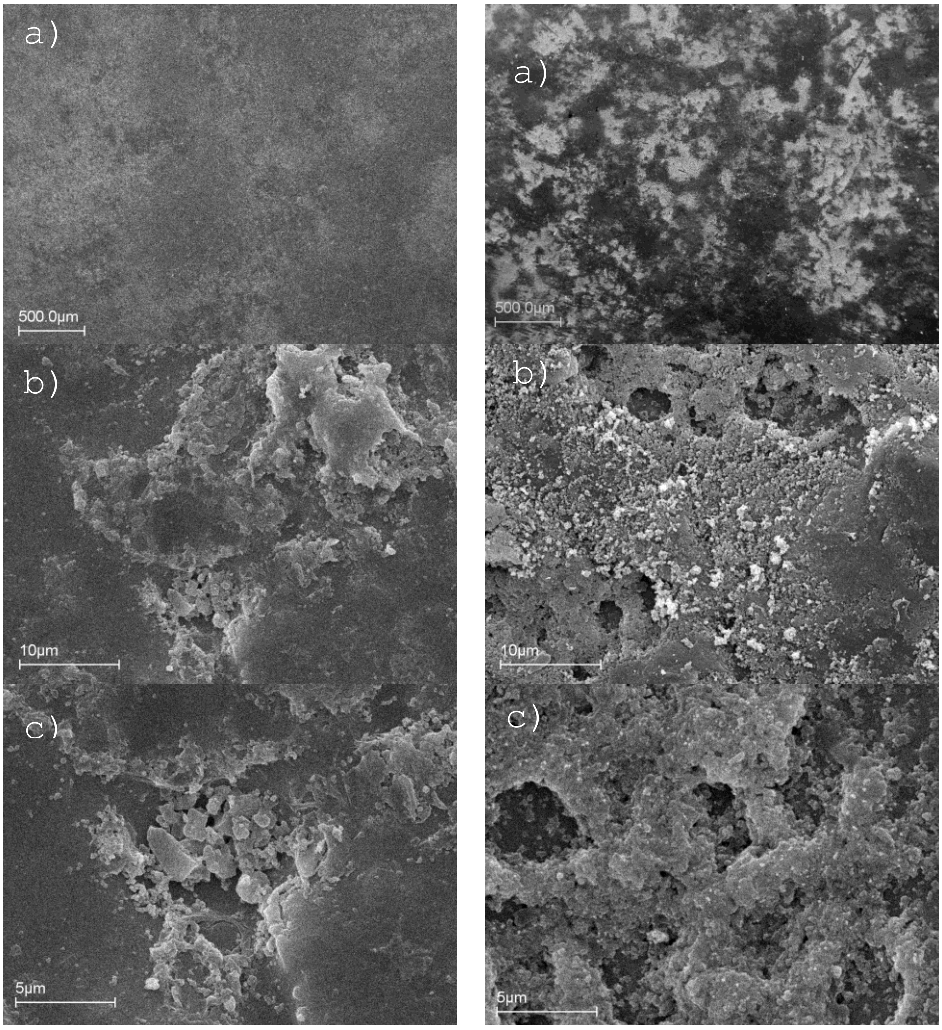


Fig.1. SEM analysis at different magnifications: a) 30X, b) 3 kX and c) 15 kX for spray deposition (on the left) and digital printing tiles (on the right).

Dark and photolysis experiments

Dark tests were performed to assess the adsorption amount on the active tiles without light exposure for the pollutants both as single molecule and in mixture. In all tests, adsorption contribution is negligible with conversion and mineralization percentages are less of 2% and zero, respectively.

Furthermore, photolysis tests were carried out to establish the effect of UV light source. Experiments point out an important instability of the starting molecules that readily convert into their by-products and after 24 hours no-presence of the pristine molecules are detected anymore, although the mineralization processes are always null, confirming the impossibility of the simple photolysis to purify water effectively.

Photocatalytic degradation of pharmaceuticals as single molecules: comparison between spray deposition and digital printing tiles. The case of distilled water.

The photodegradation results of aspirin and paracetamol in distilled water are reported in Fig.2a and b, respectively. Conversion (full symbol) and mineralization trends (empty symbol) are compared for the two photoactive samples: spray deposition and digital printing tiles.

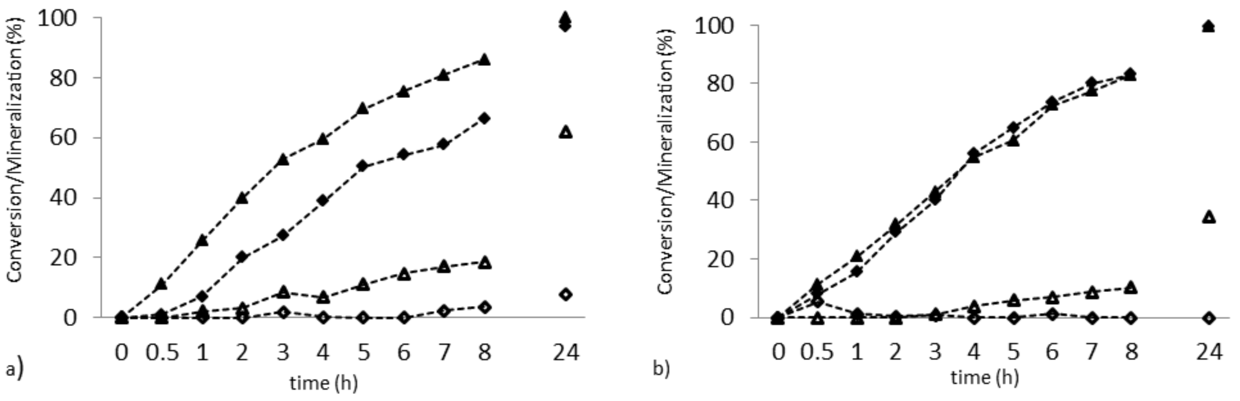


Fig.2. Photocatalytic tests of aspirin (a) and paracetamol (b) comparing the photoactive tiles: spray deposition (◆) and digital printing (▲). Conversion% (full symbol) and mineralization% (empty symbol). Deionized water.

The conversion of both drugs after 24 hours is close to 100%, regardless the type of catalytic coating and the nature of the pollutant. On the contrary, after 24 hours the corresponding mineralization values point out different photoactivity for the spray deposition and the digital printing tiles: 7% and 62% for aspirin, 0% and 35% for paracetamol, respectively. The higher TiO2 distribution and the better homogeneity of the surface coating is then able to increase the photoefficiency of the material and at the end, to effectively purify the contaminated water leading to a satisfactory degradation of the pollutants to CO_2.

Moreover, the comparison evidences a higher mineralization for aspirin than for paracetamol maybe due to different mechanism pathways. In fact, the kinetic investigations, mentioned in literature (Rincon *et al.* 2001), suggest that the paracetamol photodegradation is affected by the keto-enolic tautomeric equilibrium between hydroquinone/benzoquinone by-products that acts as holes-electrons scavenger and slows down the mineralization process (see Fig.3).

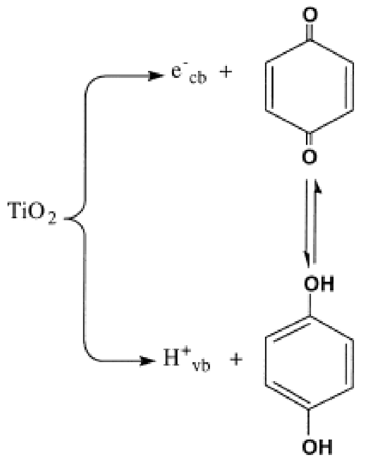


Fig.3. Keto-enolic tautomeric equilibrium between hydroquinone/benzoquinone

Photocatalytic degradation of pharmaceuticals in mixture: comparison between spray deposition and digital printing tiles. The case of deionized water

The same experiments were replicated adding aspirin and paracetamol in mixture to compare the photocatalytic performance of spray deposition and digital printing tiles: see Figures 4a and b, respectively.

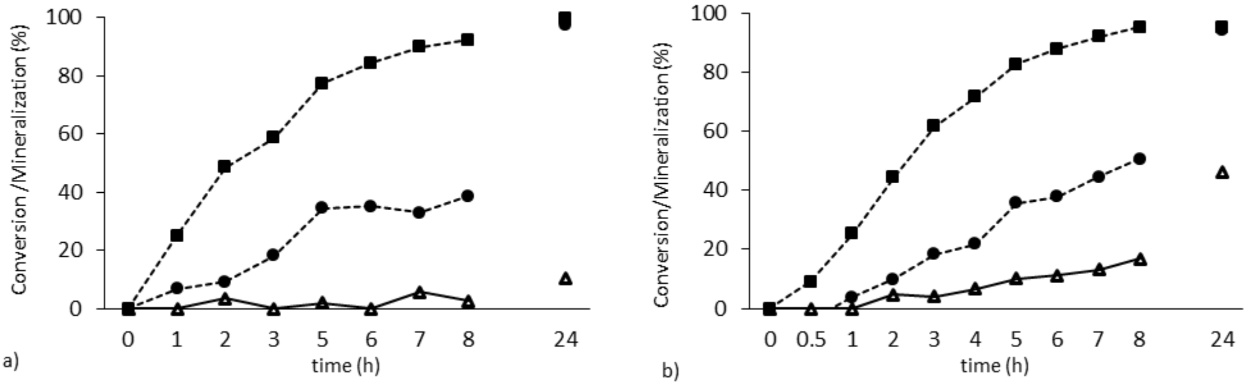


Fig.4. Photocatalytic tests of paracetamol (■) and aspirin (●) mixed performed with active tiles: spray deposition (a) and digital printing (b). Conversion% (full symbol) and mineralization% (empty symbol). Deionized water.

After 24 hours the final conversions are always close to 100% confirming the behaviour already detected in section 3.3 even in conditions of drugs mixture. It is interesting to observe that the co-presence of the two drugs points out lower rates for aspirin (circle symbol) than for paracetamol (square symbol), even if at the end, both molecules are complete degraded.

Aspirin may be involved in solvation phenomena: both acetoxy group ($-O-C(=O)-CH_3$) and carboxylic acid group (-C(=O)-OH) located in ortho position can establish hydrogen bonds leading to the production of the "so-called" "aspirin-water complex", (Karthika *et al.* 2009) as shown in Fig.5. As a results, the diffusion process towards the photoactive coating slows down and, as a consequence, the conversion of paracetamol is faster.

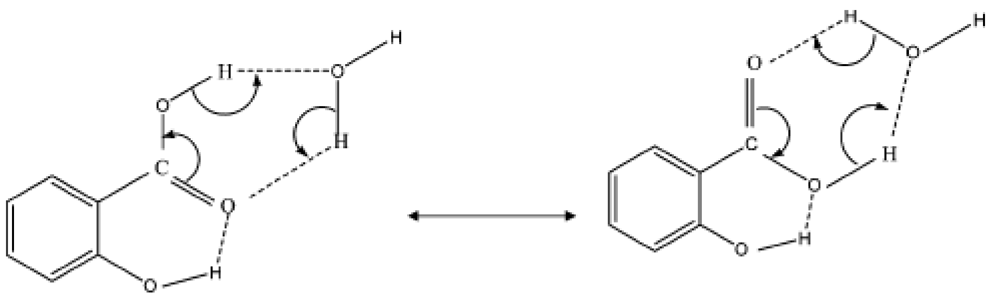


Fig.5. Resonance assisted hydrogen bonds in aspirin-water complex (aspirin: water=1:1)

The whole mineralization processes (Fig.4a and b, triangle symbol) prove the better photocatalytic behaviour of digital printing tiles (Fig. 4b), as already observed by studying the pharmaceuticals as single molecules: 10% against 46%, respectively.

Photocatalytic degradation of pharmaceuticals in presence of digital printing tile: comparison between individual and mixed pollutants. The case of tap water

The digital printing tile, that exhibited the best performance in deionized water, was further investigated in tap water in presence of aspirin (circle symbol) and paracetamol (square symbol), individually and as a mixture (Fig 6a and b, respectively). Notwithstanding the presence of the ions dissolved in water, the final conversion (full symbols) is always complete when the two drugs are investigated as single molecules; on the contrary, when they are mixed, the degradation of aspirin is a little bit slower and the final conversion is not full. As detected in deionized water, the conversion of aspirin is affected by solvation phenomena and the phenomena is still present also in tap water.

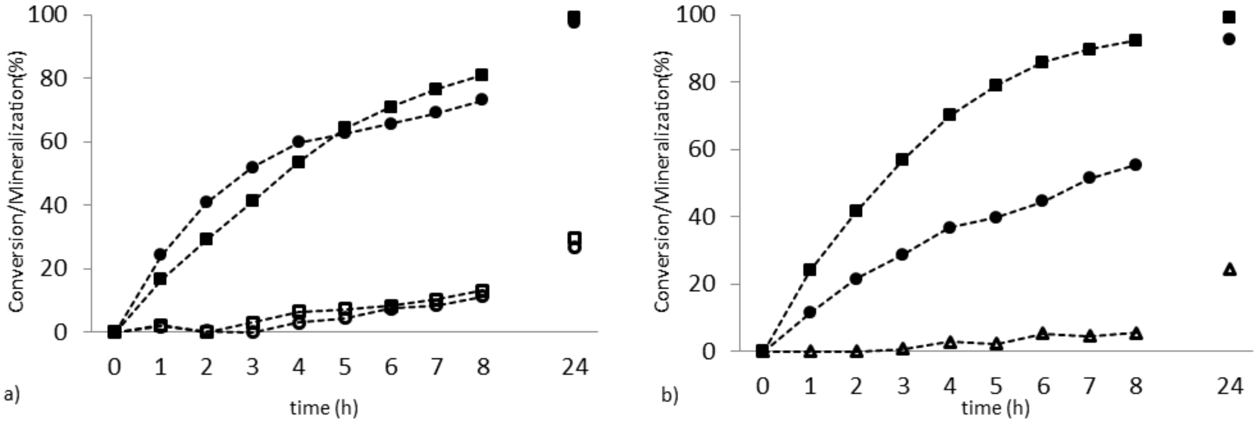


Fig.6. Photocatalytic tests of paracetamol (■) and aspirin (●) as single molecule a) and mixed (b). Conversion % (full symbol), mineralization % (empty symbol) performed with digital printing tile. Tap water.

In the case of the single pollutants, the mineralization values are probably affected by the matrix effects due to the inorganic ions present in water that act as HO^- radical scavengers. Values after 24 hours are levelled out in the 25-29% range eliminating the differences that were observed in the case of distilled water and exhibiting a net benefit in the degradation of aspirin compared to acetaminophen.

The co-presence of the two drugs limits the mineralization at 25%, more or less half than in the case of distilled water. Once more the presence of the salts is decreasing the photoactivity of the material, that however is still suitable to purify water but with slower times. However, both recovery and reuse of the tiles are very easy, avoiding any filtration and loss of photocatalytic powders in water.

CONCLUSION

The photocatalytic efficiency of commercial active porcelain grés tiles was investigated in relation to various experimental conditions. The work was performed comparing the activity of two different coatings prepared by either the classic spray deposition and the innovative digital printing methods. The selected pollutants, aspirin and paracetamol, were studied individually and as a mixture, initially in deionized water and then in tap water to compare the behavior in ideal and real conditions. The results reveal the full conversion of the drugs and the remarkable role of the photocatalytic tiles in the mineralization processes leading to harmless inorganic species. The digital printing tiles exhibit very interesting performance to fully degrade the two pollutants, mixed or not, in the different aqueous matrices and their behavior is consistent with an improved distribution and homogeneity of the TiO_2 micro-sized particles at the material surface. This new industrial active porcelain grés tiles can be successfully applied in wastewater remediation avoiding the filtration and recovery steps reducing the time and the costs of the purification treatment.

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