DETERMINATION OF THE PHOTOCATALYTIC ACTIVITY OF TiO₂ COATINGS ON CLAY ROOFING TILE SUBSTRATES - METHYLENE BLUE AS MODEL POLLUTANT

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The photocatalytically active mesoporous coatings, based on titanium dioxide sols (Degussa), of the fired clay roofing tiles substrate were prepared by using poly(ethylene glycol) (PEG) M-600 and M-4000, as the structure directing agents. The coatings were deposited using spray technique followed by thermal treatment. Photocatalytic activity of the TiO₂ coatings was evaluated by aqueous solution of methylene blue as model dye, deposited on the top of the coatings, after irradiation with UV light. The results were compared with the photocatalytic efficiency of some commercial self-cleaning products (clay roofing tiles, glass). The newly design coatings showed an interesting decolourisation performance (over 30 % after 24 h). It appeared that the procedure of photocatalytic activity determination, in the case of porous substrates, should be renewed by a pre-adsorption process.

KEY WORDS: TiO₂ coatings, clay roofing tile, photocatalytic activity

INTRODUCTION

Semiconductor photocatalysis (SPC) has attracted a great deal of attention over the last 30 years. The application of semiconductor in heterogeneous photocatalysis in order to eliminate various pollutants including many pesticides, surfactants and carcinogens in aqueous systems and in the air (1-7), has been extensively investigated. Titanium dioxide (TiO₂ - titania) appeared to be the most suitable photocatalytic semiconducting material due to its high stability toward photocorrosion and relatively favorable band-gap energy. Titania occurs in three crystalline forms: brookite, anatase and rutile. Rutile is the stable phase while anatase and brookite are metastable. Anatase TiO₂ has become the foremost semiconductor material for SPC application since it is biologically inert, mechanically robust, relatively inexpensive and highly reactive.
Photocatalytic chemical reactions occur on the surface of an SPC material. The photocatalyst generates electron/hole pairs which are capable to initiate a series of chemical reactions when it is illuminated by appropriate light source: UV light (λ≤387 nm) (4, 5, 8-11) or visible light (artificial solar and sunlight) (1, 2, 12-17). Pairs of photo-generated hole (h+) and electron (e-) induce the formation of aggressive species such as hydroxyl or superoxide radicals from the moisture and atmospheric oxygen. These species are strong enough to oxidize and decompose organic materials or smelling gas and kill bacteria (5, 11, 13, 15-17). The process is predominantly determined by the fundamental physical properties of the SPC material surface. Mesoporous coatings are predicted to have great potential to increase the photocatalytic activity by enlarging the specific surface area (18). High surface area and interconnectivity in the porous network of mesoporous coatings are desirable in order to optimize the activity of the surface and provide diffusion, charge or light transfer or reactant access into the cavities. The coatings with a greater surface area can improve the degradation rate of organic pollutants by the adsorption and the concentration of the reactants, but still allowing the latter to diffuse from the adsorption sites to the TiO2 surface.

To assess the photocatalytic efficiency of a TiO2 coating a broad range of pollutants, both of organic and inorganic nature, can be used. They can be classified into three categories:

- Dyestuffs (19, 20),
- Organic compounds (21),
- Inorganic gases (22).

Dyes are degraded by TiO2 under the influence of UV or solar light. The decomposition is assessed by decoloration measurements (color removal ratio), as well as chromatographic investigations. The widespread application of, for example, methylene blue (MB) originates from the fact that it is mainly nontoxic and convenient for the use as a dye. MB exhibits strong absorption in the visible light (λ_{max} =664 nm; ε_{664} = 7.4×10^4 M^{-1} cm^{-1}) but not in the UVA region. This fact presents the perceived effectiveness of the MB test, which is considered by the International Organization of Standardization (ISO) as a standard test for photocatalytic surfaces (16, 23). However, the assessment of decomposition processes of dyes by decoloration measurements is still a subject of discussion.

The present research was focused on obtaining mesoporous coatings using TiO2 and poly(ethylene glycol) (PEG) of different molecular weight, as a structure directing agent applied on ceramic roofing tile surface. The functionality of these coatings have been tested by the photocatalytic decomposition of MB in aqueous solution. These values were compared with the activity of the commercial products (clay roofing tiles and glass samples). Major attention has been devoted to the selection of a suitable sample preparation. Namely, ceramic roofing tiles as a porous material, without photocatalytic coating, also adsorb a certain quantity of MB solution decreasing its concentration. In order to assess the contribution of the photocatalytic activity of the prepared mesoporous titania coating, the photocatalytic tests were modified compared to the tests where a non-porous substrate was used. The precursory adsorption of methylene blue was established until the adsorption process of the dye was complete. After that the decomposition rate of the dye under the UVA light irradiation (photocatalytic activity) was determined by recording its absorption spectrum.
EXPERIMENTAL

**Photocatalytic dispersion.** The photocatalytic dispersion, sol, was prepared by mixing 2.5 mass % TiO2 aqueous (deionised water) colloidal dispersion (VP Disp.W 2730 X, Degussa, Frankfurt, Germany) and PEG (HOCH2(CH2OCH2)nCH2OH) with molecular weight 600 (M-600) or 4000 (M-4000), (Baker, Germany). Titania particle size in colloidal dispersion was reported to be (d-50= 50-100 nm), dry matter content 30.0 +/-1.0 mass%, and pH value 5-7.

**Tile substrate.** The clay roofing tiles produced in the industrial conditions (a.d. Polet, member of Nexe group, Novi Bečej, Serbia) were cut in the form of square-shaped slabs (dimensions 3.5 x 3.5 x1.5 cm) and used as substrates for photocatalytic coating preparation. The used raw material for the tile production was based on illite-kaolinite clay material and carbonates (dolomite, calcite).

**Preparation of TiO2 layer on clay roofing tile substrate.** The photocatalytic sol was frequently stirred in order to obtain stable coating solution. The stability of the suspension is essential to achieve the necessary consistency.

Three layers of the photocatalytic sol were deposited by spray technique on the top of the clay roofing tiles. Drying of the photocatalytic sol layers lasted 30 min at 25°C and 50% air RH. They were subsequently heated in an oven at: 290°C for 30 minutes, case of the sol based on 2.5 mass% TiO2 and PEG 600 (marked as NM 600), and at 400°C for 30 minutes, the sol based on 2.5 mass% TiO2 and PEG 4000 (marked as NM 4000).

**Photocatalytic activity of TiO2 coatings.** The photocatalytic activity of the TiO2 coatings was evaluated by examining the discoloration of the methylene blue, in the procedure adjusted to porous substrate, as follows.

As first, the degree of adsorption of the dissolved MB molecules, by the surface of the mesoporous titania coatings and tile substrate, was measured by a pre-adsorption test. A cylindrically shaped glass cell with the inner diameter of 3 cm and a height of 6 cm was attached to the substrate using silicon glue. Both the test cell and substrate are marked as a test sample. The concentration of MB for the pre-adsorption test and for the photocatalytic test was 20 and 10 μmol/L, respectively. Twelve milliliters of the MB for the pre-adsorption test were poured into the test cell. The part of the tile was drowned into the MB solution of the same concentration. The adsorption of the MB (20 μmol/L) by the tile sample proceeded in the dark for 12 h. The procedure was continued in the dark with the test solutions of MB (10 μmol/L) for 24 h up to 36 h (until the adsorption of the dye was completed). The adsorption was considered complete if the differences in the concentration of MB measured after 30, 60, 120 and 150 min were less than 5%.

In the above procedure, the adsorption of the dye was complete and the test samples were irradiated with UVA light (Osram Eversun lamp / I= 0,67 mW/cm²/ distance between the UV lamp and the reactor 18 cm) for 1.5, 2.5, 3.5 and 24 h, Fig. 1a and 1b. The emission spectrum of the lamp light and absorption spectrum of MB are shown in Fig. 2. The maximum irradiation of the lamp is in the range of 320-380 nm. It is evident that the absorption spectrum of MB is not in the range of the emission spectrum of the lamp.
The photocatalytic activity of the materials was monitored on a UV/VIS spectrophotometer (Evolution 600 / Thermoscientific, England / water as the reference sample) by measuring absorption spectra of MB ($\lambda$=664 nm) as a function of the irradiation time.

Photocatalytic activity of the TiO$_2$ coatings was calculated using the relation 1:

$$\text{TiO}_2 \text{ activity} = \left( \frac{c_0 - c}{c_0} \right) \times \left[ \frac{c_1}{c_0} \right] \times 100 \quad [1]$$

where $c_0$ is the concentration of the test solution of MB before irradiation; $c$ is the concentration of MB after UV irradiation, and $c_1$ is the concentration of MB after the pre-adsorption test.

The concentrations $c$ and $c_1$ were determined from the calibration curves showing the dependence of the absorbance at $\lambda_{\text{max}}$ (664 nm) of MB solutions as a function of the concentration of MB solutions.

The above procedure was applied on the clay roofing tile samples with mesoporous coatings (NM 600, NM 4000) and clay roofing tiles without catalyst-mesoporous coating (marked as N), as well as on the commercial self-cleaning products (clay roofing tile-E / Germany; glass-SG / France). For each experiment four measurements were performed.
RESULTS AND DISCUSSION

The clay roofing tiles (a.d. Polet, member of the Nexe group) are complex materials with total porosity of about 13%. During the firing procedure stable secondary mineral phases as gehlenite, anortite or diopside, are formed. Besides stable mineral phases, a certain amount of "active centers" are present on the porous tile surfaces. These centers can influence different adsorption processes. Evidently, the porosity of the tiles increases the consumption of the applied titania dispersion prepared for self-cleaning and decreases the photocatalytic activity of the formed titania coating. The mesoporous TiO2 coatings based on PEG 600 (NM 600) and PEG 4000 (NM 4000) have similar surface area (≈100 cm²/g). Both coatings have an average pore size diameters about 10 nm. In the case of the NM 4000 samples the pore size distribution was wider, with a higher amount of small pores (24). The thickness of the coatings NM 600 and NM 4000 was about 3 μm. Fig. 3 shows the SEM micrograph of the sample NM 4000 (thickness about 3 μm).

![SEM micrograph of the mesoporous TiO2 coating NM 4000 (x5000)](image)

The photocatalytic activities of the TiO2 coatings were evaluated by using the aqueous solution of the MB, according to DIN 52980:2007-11 (25) and ISO/DIS 10678 (23). The photocatalytic activity of the mesoporous coatings can be defined as a two step process: pre-adsorption (elimination of the influence of MB adsorption) (20, 26, 27), and MB irradiation test (determination of the photocatalytic activity). Maximum absorption appears at λ=664 nm and gradually decreases during the irradiation time. Like many thiazine dyes, MB has a tendency to dimerise. The dimer of MB, (MB)₂, has an absorption maximum at 614 nm (28). As a consequence of dimerization the size of the MB molecules increases, which can be an important step in the catalysis since diffusion towards and from catalyst surface is an important step in the decolorization of MB solution. The decrease of the absorption maximum at 614 nm indicates that the photocatalytic coating possesses a photonic efficiency for degradation, Fig. 4. The decrease of the concentration of MB solution at 614 nm and 664 nm, during irradiation time, clearly shows that the sample NM 600 is active.
Fig. 4. Dependence of the absorbance spectra of MB solution (10 μmol/L) in contact with NM 600 on UVA irradiation time

The photocatalytic activities of the samples were calculated from equation 1. The activities of the samples NM 600, NM 4000, were compared with the values for the commercial self-cleaning products: glass- SG, clay roofing tiles-E and clay roofing tiles without mesoporous TiO₂ coating (N), Fig. 5.

Fig. 5. Photocatalytic activity of tested samples during the irradiation time

Several conclusions can be drawn from Fig. 5. Firstly, no significant differences in the activity were obtained after 24h irradiation time of the samples NM 600, NM 4000 and E. The activity of the commercial glass-SG was lower in comparison with the samples NM 600, NM 4000 and E. Secondly, these differences are greater up to 3.5 h of irradiation. These results demonstrate the fact that samples NM 600 and NM 4000 are the most active ones. The MB molecules were probably more adsorbed (24) in the case of these samples due to the fact that the coatings have a higher surface area and, consequently, the decrease of the MB concentration in aqueous solution was more pronounced. Later (after 24h irradiation), a deactivation phenomenon was observed. The active catalyst sites were probably blocked by the formation of the intermediate products and, consequently, the photocatalytic activity of these systems was decreased. This conclusion is in concordance with our previous investigation (29). Namely, the samples NM
and NM 4000 can be partially regenerated by washing with water (rainfall simulation).

A control photocatalytic experiment, to evaluate the dye decolorization, was carried out with the irradiated samples without catalyst (N). The obtained results indicate that decolorisation of the MB was not negligible, Fig. 5. It seems that MB is not an ideal model pollutant, probably the surface of the clay roofing tiles has also some redox potential. More reliable values of the photocatalytic activity could be the difference between the activity values of NM 600 and N samples / NM 4000 and N samples. Unfortunately, this procedure was not possible to apply in the case of the commercial products (the reference samples for these experiments were missing).

CONCLUSION

The photocatalytic activity of the samples based on 2.5 mass% TiO$_2$ and PEG 600 (NM 600), 2.5 mass% TiO$_2$ and PEG 4000 (NM 4000), clay roofing tiles without catalyst - mesoporous coating (N), commercial roofing tiles (E) and commercial glass (SG) were determined as a two-step process: pre-adsorption, and photocatalytic test. Their efficiency in regard to the MB degradation was found to vary significantly in the laboratory conditions. The activities of the mesoporous coatings NM 600 and NM 4000 were higher up to 3.5 h of irradiation time than the activities of the commercial samples. After 24h of irradiation the efficiency of the prepared mesoporous coating NM 600, NM 4000 was equal to the values of the commercial self-cleaning ceramic roofing tiles (E), while the activity of the commercial self-cleaning glass (SG) was significantly lower.

This study suggested that porous substrate without titania coating, due to an adsorption process, also undergoes a decolorization phenomenon of the MB aqueous solution. The MB test should include the pre-adsorption test, especially in the case of porous materials such as ceramic roofing tiles.

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REFERENCES


ОДРЕЂИВАЊЕ ФОТОКАТАЛИТИЧКЕ АКТИВНОСТИ TiO₂ ПРЕВЛАКА НА ЦРЕПУ КОРИШЋЕЊЕМ МЕТИЛЕН ПЛАВОГ КАО МОДЕЛ ПОЛУТАНТА

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Фотокаталитички активне мезопорозне превлаке нанете на површину глиненог црепа направљене су од сола титанијум диоксида (Degussa, Germany) и поли(етилен гликола-PEG) M-600 и M-4000 који је носилац мезопорозне структуре. Превлака је нанета коришћењем спреј технике и термичког третмана. Фотокаталитичка активност TiO₂ превлака је проценета коришћењем метilen плавог као модел боје, постављене на превлаку, након зрачења UV зрацима. Резултати су поређени са резултатима фотокаталитичке активности неких комерцијалних производа (глинени цреп, стакло). Новоформирана превлака је показала значајан ниво обезбојавања раствора (преко 30% после 24h). Установљено је да поступак одређивања фотокатализичке активности за случај порозног црепа би требало да буде иновиран увођењем процеса предадсорпције.

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