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ENVIRONMENTAL EFFICIENCY OF UV-ACTIVATED TiO_2-MODIFIED ACRYLIC SELF-CLEANING SURFACES

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Abstract: Raising awareness of the importance of protecting the environment generates ever-increasing efforts of chemists and material scientists who seek new chemical compounds, production methods, and new types of surfaces and materials with self-cleaning abilities. Taking into consideration the data on increasing pollutant levels in the environment, materials that degrade pollutants could be an acceptable, sustainable solution to improve self-cleaning materials, especially when functionalizing large surfaces characteristic of building materials. The development of building materials that degrade polluting chemicals and carry out the mineralization of pollutant loads has now become a necessity. This work aimed to analyze the environmental performance of TiO_2-modified acrylic surfaces under UV–LED irradiation through the oxidative processes taking place on the illuminated surfaces. The simple approach of synthesis yielded highly affordable self-cleaning surfaces. The self-cleaning properties of these surfaces were tested against three frequently used textile dyes, rhodamine B, methylene blue, and methyl orange. It was demonstrated that rhodamine B was still present after 10 h of irradiation, while methylene blue and methyl orange were successfully self-cleaned after 3 h and 5 h, respectively.

Keywords: Dyes, self-cleaning surfaces, environmental pollution, photocatalysis.

1. INTRODUCTION

In the last few decades, the global community has gradually shown a substantial interest in environmental quality [1] . A wide variety of concerns, from purely aesthetic and ethical ones to those related to valuable forms of aquatic and wildlife, has prompted the development of sophisticated monitoring programs aimed at achieving a better understanding of the current state of the environmental resources [2]. As a result of this effort, serious pollution problems have been repeatedly detected in several parts of the planet. This is associated with the particular increase in the use of industrial materials of anthropogenic origin [3]. Among these materials, one of the most important classes is synthetic organic dyes, a subfamily of thousands of organic compounds that are not only widely utilized in industries such as textiles, paper, food, and cosmetics but are almost always toxic (hence considered extremely hazardous) towards aquatic life forms if inappropriately discarded [4,5]. The amount and nature of discharges of dyes depend on many factors, but the exhaustive control and many of these discharges are mediated by legislation [6]. The presence of dyes in both industrial and domestic effluents is a well-known fact, and their undesirable consequence is the increasing need for hazardous waste treatment deriving from the dye industry [7]. In fact, the production of synthetic dyes and related pigments increased, and with this production, its proportional discharge has generated significant environmental contaminations [8,9].

Self-cleaning is the property of a surface to shed water or dirt and be free of contaminating materials such as dust, dirt, dyes, and microorganisms under environmental conditions such as sunlight irradiation and rainwater exposure [10,11]. It is related to the surface properties of a material. The hygiene of material surfaces is becoming an increasingly important aspect in a wide range of technological applications, including windows and facades, automobiles, self-cleaning of solar cells, and exterior material of buildings [12,13].

In recent years, self-cleaning materials have attracted extensive attention owing to advancements in a wide range of various fields, such as biological self-cleaning [14,15] and physical or chemical artificial self-cleaning, using numerous nanoparticles [16]. These methods require exposure to sunlight to support the fast decomposition of any unwanted impurities on the surface and then sustain the decomposing of the present products [17]. These technologies are associated with limitations with respect to demonstrating hydrophobic and photocatalytic properties simultaneously [18].

This work aimed to employ a strategy to produce surfaces with significant self-cleaning properties by coating the aluminium (Al) foil with white acrylic paint mixed with TiO_2 Hombikat. The environmental performance of TiO_2-modified acrylic surfaces was tested under UV–LED irradiation through the oxidative processes taking place on the illuminated surfaces. The self-cleaning properties of obtained tiles were tested against three dyes that are widely used and, by their inappropriate disposal, represent environmental threats - rhodamine B, methylene blue, and methyl orange. While testing the self-cleaning properties, dyes were dropped on coated surfaces, after which the samples were exposed to UV–LED irradiation to activate photocatalytic nanoparticles and initiate the degradation of dyes. Rhodamine B was still present after 10 h of irradiation, while methylene blue and methyl orange were successfully self-cleaned after 3 h and 5 h, respectively. Water addition and simulation of environmental conditions with rainfall contributed to the lower self-cleaning efficiency.

2. MATERIALS AND METHODS

2.1. Chemicals and solutions

Used chemicals were of reagent grade and were employed without further purification. Chemicals utilized were rhodamine B ($C_{28}H_{31}ClN_2O_3$, >99.9%, Merck, Darmstadt, Germany), methylene blue ($C_{16}H_{18}ClN_3S$, >99%, Merck, Darmstadt, Germany), and methyl orange ($C_{14}H_{14}N_3NaO_3S$, >99.9% Kemika, Zagreb, Croatia), ethanol (C_2H_6O, >99.8%, Merck, Darmstadt, Germany), acrylic concrete paint (Betokril, Poly, Šid, Serbia), TiO_2 Hombikat (100% anatase, Sigma-Aldrich, specific surface area 35–65 m^2/g). Each solution was made using ultrapure water (pH 6.56, κ = 0.055 μS/cm, total organic carbon TOC < LOD). The concentration of dye in the aqueous stock solution was 0.05 $mmol/dm^3$.

2.2. Materials for Synthesis

Commercial Al foil was used as a solid surface for applying TiO_2-modified acrylic paint with 1.0 mg/cm^3 TiO_2 Hombikat as a photocatalyst. Al foil was first cleaned with ethanol. The mixture of TiO_2 and acrylic paint was made by adding the appropriate amount of TiO_2 to acrylic paint, after which this mixture was homogenized. Then, the surfaces were coated with a TiO_2 acrylic paint layer (Figure 1) [19]. The coated samples underwent air drying and were then subjected to a 15 min treatment in an oven at 200 °C to enhance adhesion to the substrate [20].

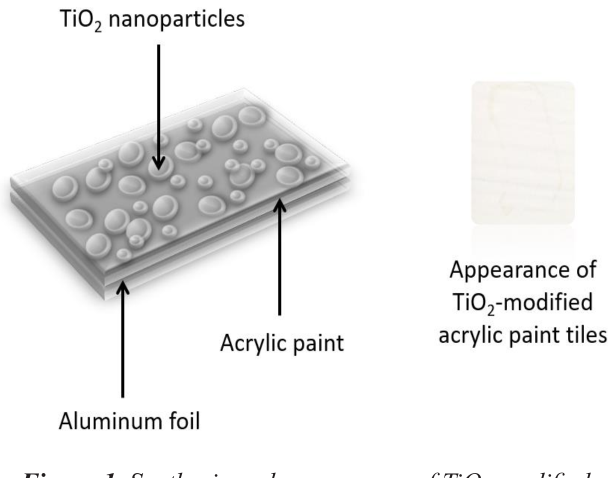

Figure 1. *Synthesis and appearance of TiO_2-modified acrylic self-cleaning surfaces.*

2.3. Self-cleaning experiments

During self-cleaning experiments, coatings were placed on a flat surface, and an irradiation beam was focused on them. 10 µL and 20 µL of dye solutions were applied to the surface of the coatings before irradiation. In one series of experiments, 2 µL of water was added to the coating surfaces after each hour of irradiation. Tiles were irradiated for 10 h using UV–LED irradiation (Enjoydeal, China, type MR16 AC 85-265V/12). UV and Vis radiation intensities of the lamp were $7.5\cdot10^{-2}$ W/cm^2 and $74.4\cdot10^{-2}$ W/cm^2, respectively. The distance between the tiles and the irradiation source was 50 mm. The radiation energy fluxes were measured using a Delta Ohm HD 2102.2 (Padova, Italy) radiometer, which was fitted with the LP 471 UV (spectral range 315–400 nm) and LP 471 RAD (spectral range 400–1050 nm) sensors.

3. RESULTS AND DISCUSSION

Self-cleaning coatings are considered one of the potential novel approaches to mitigate polluting substances and improve the durability of buildings [21]. The self-cleaning capabilities of prepared coatings were tested on three dyes (rhodamine B, methylene blue, and methyl orange), applying two different dye volumes (20 µl and 10 µl) to assess effectiveness across varying contamination levels. Coatings with applied dyes were irradiated during a 10 h period with UV–LED irradiation to evaluate the tiles' self-cleaning properties.

From Figure 2, we can see that the most efficient self-cleaning was achieved in the case of methylene blue, wherein this dye was removed after 3 h. Methyl orange was self-cleaned after 5h. However, rhodamine B was still present on the coating surface even after 10 h of irradiation, but, notably, the dye color was significantly faded.

In further experiments, 2 µL of water was added to the surfaces after each hour of irradiation (Figure 3). Therefore, self-cleaning properties were estimated in real environmental conditions in case of rainfall. The addition of water contributed to the slower self-cleaning of dyes due to water evaporation and the inability of irradiation to be in contact with the same volume of dyes. Methylene blue was removed after 6 h, whereas methyl orange necessitated 8 h. Traces of rhodamine B were still present on the coating surfaces after 10 h, and as can be seen, they were less faded (Figure 3) compared to Figure 2, wherein water was not added.

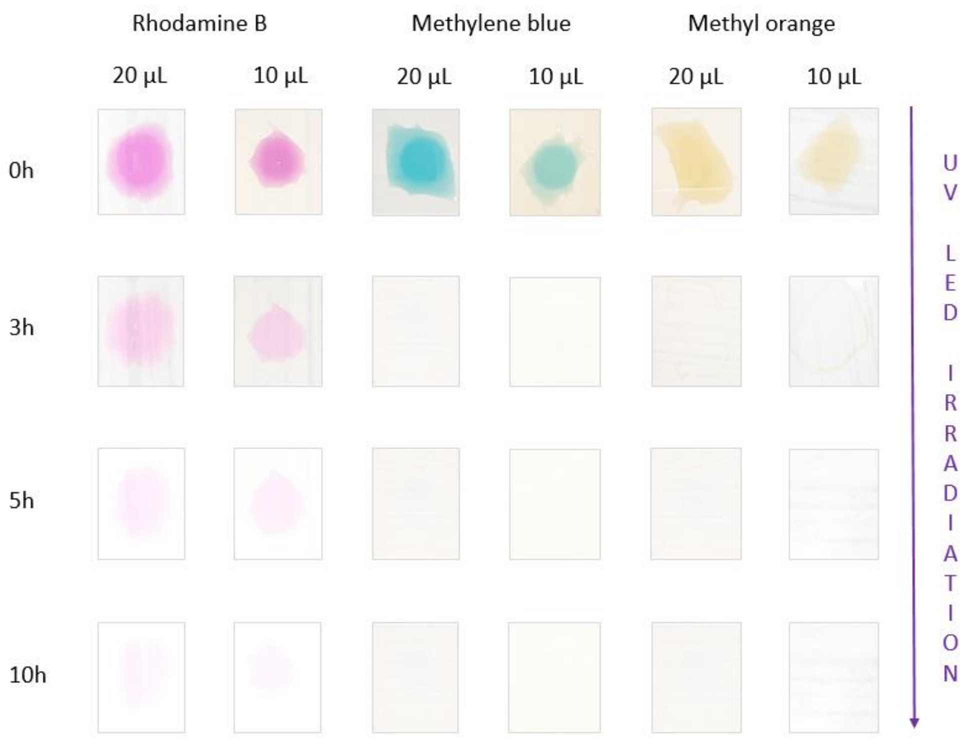

Figure 2. *Dye removal using self-cleaning TiO_2-modified acrylic paint coatings.*

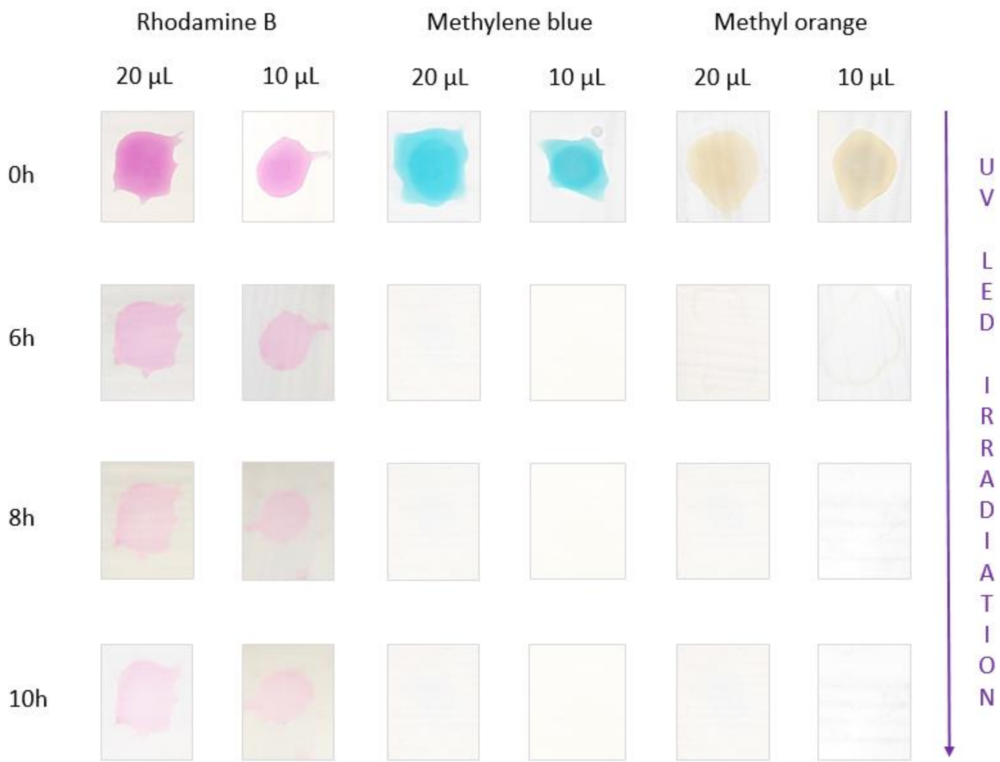

Figure 3. *Dye removal using self-cleaning TiO_2-modified acrylic paint coatings, 2 µL of ultrapure water was sprayed on the sheet surface after each hour of irradiation.*

CONCLUSION

In this work, we employed a simple strategy to produce surfaces with self-cleaning properties. Synthesis was performed by coating the aluminum foil with white acrylic paint mixed with TiO_2 Hombikat. The self-cleaning performance of TiO_2-modified acrylic surfaces was tested under UV–LED irradiation with and without the addition of water. Self-cleaning properties were tested against three frequently used industrial dyes (rhodamine B, methylene blue, and methyl orange), which were considered significant environmental threats. Methylene blue and methyl orange were successfully self-cleaned after 3 h and 5 h, respectively. Rhodamine B was the most persistent color, and it was still present after 10 h of irradiation, but the dye color was significantly faded. The addition of water contributed to the slower self-cleaning of dyes, and in this case, methylene blue was removed after 6 h, methyl orange necessitated 8 h, while rhodamine B was still present on the coating surfaces after 10 h.

The investigation into self-cleaning coatings is crucial for reducing pollution and increasing the lifetime of building materials. These coatings can degrade pollutants, contributing to cleaner urban environments and healthier living conditions. Additionally, self-cleaning surfaces require less maintenance, reducing the frequency and cost of cleaning while extending the lifespan of buildings and infrastructure. This research also provides insights into optimizing the performance of self-cleaning coatings under various environmental conditions, such as different dye contaminants and the presence of water, making them more effective and practical for real-world applications.

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ЕКОЛОШКА ЕФИКАСНОСТ УВ-АКТИВИРАНЕ TiO_2-МОДИФИКОВАНЕ АКРИЛНЕ САМОЧИШТЕЋЕ ПОВРШИНЕ

Подизање свести о значају заштите животне средине генерише све веће напоре хемичара и научника који траже нова хемијска једињења, методе производње и нове врсте површина и материјала са способношћу самочишћења. Узимајући у обзир податке о повећању нивоа загађујућих материја у животној средини, материјали који разграђују загађујуће материје могли би бити прихватљиво, одрживо решење за побољшање самочистећих материјала, посебно при функционализацији великих површина карактеристичних за грађевинске материјале. Развој грађевинских материјала који разграђују хемикалије које загађују и врше минерализацију загађујућих материја сада је постао неопходност. Овај рад је имао за циљ да анализира еколошке перформансе TiO_2-модификованих акрилних површина под УВ–ЛЕД зрачењем кроз оксидативне процесе који се одвијају на осветљеним површинама. Једноставан приступ синтези дао је високо приступачне самочистеће површине. Својства самочишћења ових површина тестирана су у односу на три најчешће коришћене текстилне боје, родамину Б, метилен плавом и метил наранџастом. Показано је да је родамин Б и даље присутан након 10 сати зрачења, док су метилен плаво и метил наранџасто успешно самоочишћене након три, односно пет сати.

Кључне речи: Боје, самочистеће површине, загађење животне средине, фотокатализа.

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