Preparation and Study of Photocatalytic Hydrophobic Surface-Modified TiO_2 Coatings in Degradation of *E. coli* and Various Azo Dyes

Kazemi Hakki, Hamid*+

Department of Chemical Engineering, Faculty of Engineering, Soran University, Soran, Erbil, Kurdistan Region, IRAQ

Ghaderi, Aref

Department of Civil Engineering, Faculty of Engineering, Soran University, Soran, Erbil, Kurdistan Region, IRAQ

Zeynali, Rahim

Technical and Vocational University, Urmia, I.R. IRAN

Seyyedbagheri, Hadi; Alinezhad Avalzali, Hossein

Chemical Engineering Faculty, Sahand University of Technology, Sahand New Town, Tabriz, I.R. IRAN

Ahmed, Shahla Zubair

Department of Chemical Engineering, Faculty of Engineering, Soran University, Soran, Erbil, Kurdistan Region, IRAQ

ABSTRACT: *In this research, TiO_2 nanoparticles were synthesized by sol-gel method and coated on the tile by using the Doctor Blade method. The TiO_2 hydrophobic coatings were prepared by applying oleic acid and an organic binder on the tile substrate. The XRD, FESEM, Contact Angle, and FT-IR analyses characterized the manufactured coatings. According to the XRD pattern, the synthesized nanoparticles have good crystallinity, and two anatase and rutile phases have formed. The contact angle analysis showed that the contact angle increased by surface modification by using oleic acid. The antibacterial and photocatalytic activity of the coatings were evaluated in the decomposition of Escherichia Coli in various concentrations of bacteria and various dyes. The results confirmed the good antibacterial and photocatalytic activity of TiO_2 coatings. The stability and durability of the coatings were examined by applying the salt spray test, Shore D test, and ultrasonic bath. The coatings revealed good anti-corrosion properties, and the hydrophobicity of the coatings was preserved after the salt spray test.*

KEYWORDS: *Hydrophobic coating; TiO_2 nanoparticles; Anti-corrosion coating; photocatalytic and antibacterial activity; Durability and Stability.*

* *To whom correspondence should be addressed.*
+E-mail address: ha_kazemi@sut.ac.ir
1021-9986/2023/4/1210-1220 11/$/6.01

INTRODUCTION

Due to the growing population, the rapid spread of pathogenic microorganisms and their persistence on different surfaces has led to the fast transmission of the disease among people in society [1, 2]. On the other hand, due to the effects of chemical disinfectants on human health and the destruction of the strength and beauty of surfaces, researchers decided to use self-cleaning, antibacterial, and antimicrobial coatings to prevent disease spread and decrease the chemical disinfectant effects [3]. On the other hand, the entry of dyeing and textile wastewater into surface water sources annihilates the water ecosystems and also threatens food security. Azo dyes are one of the largest water pollutants with high stability in the environment and causing adverse health effects [4]. They cause skin allergies, carcinogenic and pulmonary diseases. Therefore, it is essential to degrade dyes using effective and inexpensive methods without any dangerous residue. However, azo dyes containing different materials have been applied for various optical and electronic applications such as dye-sensitized solar cells, optical switching, etc. [5]. So that in the last two decades, dye-sensitized solar cells (DSSCs) have been the focus of the research community, because they are considered as suitable alternatives for the next generation photovoltaic devices [5].

A wide range of organic compounds are used in different pharmaceutical products, which effects have been widely investigated. *Ahmad et al*. studied the antibacterial activity of acylated oligosaccharides (integrisides A and B) against four pathogenic bacterial strains, as well as four fungal strains. Both the compounds revealed remarkably similar results to the standard drugs imipenem and miconazole [6]. *Aktas Anil et al*. prepared twelve novel 1 H- 1,2,3-triazole derivatives and evaluated the inhibition effects of these compounds on AChE, ALR2, and hCA I and II. Enzyme assay study determined that, compound 58 (4-Br) showed strong inhibition against ALR2, AChE, and hCAII, while compound 51 (4-F) showed the best inhibition against hCAI [7]. Due to the disadvantages of organic compounds used for disinfection, including toxicity to the human body, interest in inorganic disinfectants such as metal oxide nanoparticles is increasing [8].

A combination of nanotechnology and pharmacology has helped the production of novel antimicrobial compounds to control resistant microorganisms of fungi and bacteria. Specially, TiO_2 nanoparticles have been considered as efficient antimicrobial compound owing to their photocatalytic intrinsic, large surface-to-volume ratio, safe physicochemical properties, high aspect ratio, and reactivity [9].

In recent years, the use of self-cleaning antibacterial coatings with the help of nanotechnology has been significantly used by researchers.

Self-cleaning coatings contain nanoparticles such as TiO_2, ZnO, WO_3, Bi_2O_3, etc., that can cause degradation of pollutants in the presence and absence of light[10]. These coatings are stabilized by different techniques such as dip-coating, spin coating, spraying, Doctor blade method, etc., on different substrates such as metal, tile, fabric, and various surfaces [11]. Self-cleaning antibacterial nanocoatings are among the important achievements of nanotechnology in air purification, wastewater treatment, the construction industry, etc. [12]. Self-cleaning coatings used in building facades will be very practical and effective in air purification and significantly reduce the adsorption of pollution and the destructive effect of ultraviolet light on building facades [13, 14]. The use of these coatings in the construction industry creates an environment free of pollution and pathogens, long life of the facade and equipment prevents the accumulation of moisture and corrosion on surfaces, etc. Self-cleaning antibacterial nanocoatings, which can also be hydrophobic, are defined based on the contact angle of the liquid droplet with the solid surface [15]. If this angle is more than 90 degrees, the surface is called hydrophobic, and the hydrophilicity of these coatings is defined as an angle less than 90 degrees [16]. TiO_2 and ZnO are among the most widely used photocatalytic nanoparticles used in self-cleaning antibacterial coatings. TiO_2, due to its high thermal stability, non-flammability, poor solubility, non-toxicity, and natural origin, has various applications such as air purification, wastewater treatment, etc. [17]. TiO_2 structural phases are brookite, anatase, and rutile, which the anatase phase has more photocatalytic activity than the other two phases [17]. ZnO has the wurtzite crystalline structure and, in comparison to TiO_2, has better light absorption and photocatalytic activity. Zinc oxide is non-toxic, non-flammable, high thermal stability and natural origin [18]. ZnO Disadvantages can include low photocatalytic activity under visible light and corrosion in acidic environments [19]. *Kumar et al*. synthesized the ZnO nanorods using a two-step successive ionic-layer

adsorption and reaction method and chemical bath deposition without any surface modification and pretreatment. The synthesized ZnO nanorods showed good hydrophobic behavior (contact angle=160) and good anti-reflective properties [20]. In the research conducted by *Najafidoust et al*., floating Fe-ZnO/SA (Fe-ZnO over the hydrophobic silica aerogel) synthesized by the precipitation impregnation method and used to degrade suspended BTX. Their research showed that the sample with 20% silica aerogel had good hydrophobicity and photocatalytic activity in the degradation of BTX [21]. In order to synthesize hydrophobic silica nanoparticles, *Dargahi Zaboli et al*. used long-chain 1-octa decanol as a surface modifier. Their research revealed that with increasing the concentration of the modifier agent, the contact angle increased to 63° [22].

Gurav et al. used low-energy surface materials such as stearic acid to prepare ZnO hydrophobic self-cleaning coatings. Their study disclosed that stearic acid caused to increase in the contact angle between water droplets and the surface and decreases the surface's wetting [23].

Kazemi Hakki et al. studied the photocatalytic activity of TiO_2 coatings in photodegradation of methylene blue. For this purpose, they synthesized TiO_2 photocatalyst by the sol-gel method and stabilized nanoparticles on glass plates by using the dip-coating technique. Their research revealed that the prepared coatings had high photocatalytic activity in decomposing methylene blue from wastewater [17]. *Najafidoust et al*. studied the effect of diethanolamine as a stabilizer on the morphology, roughness, and photocatalytic activity of ZnO coatings in the photocatalytic degradation of methylene blue. Their research indicated that the molar ratio of diethanolamine has an influential role in the relative roughness and photocatalytic activity of coatings which by increasing the molar ratio of diethanolamine from 1 to 2, the photocatalytic activity of coatings decreases [11].

In the present study, TiO_2 hydrophobic coatings were synthesized by the sol-gel method and coated on the tile by the Doctor Blade method. Its hydrophobic and antibacterial properties were investigated. In this research, an alcoholic solution of oleic acid was used to modify the surface of TiO_2 nanoparticles and prepare the hydrophobic coatings. In order to increase adherence of the coatings to the substrate, unsaturated polyester resin as an organic binder was also used in addition to acid washing the substrates. Pure TiO_2 has good photocatalytic properties, high Thermal stability, and high corrosion resistance, which, in addition to better degradation of pollutants under light, unlike ZnO, does not corrode in acidic environments. The mentioned properties and surface modification of TiO_2 with oleic acid lead to the preparation and production of efficient and cheap photocatalytic hydrophobic coatings with high durability and stability compared to hydrophobic coatings based on silanes.

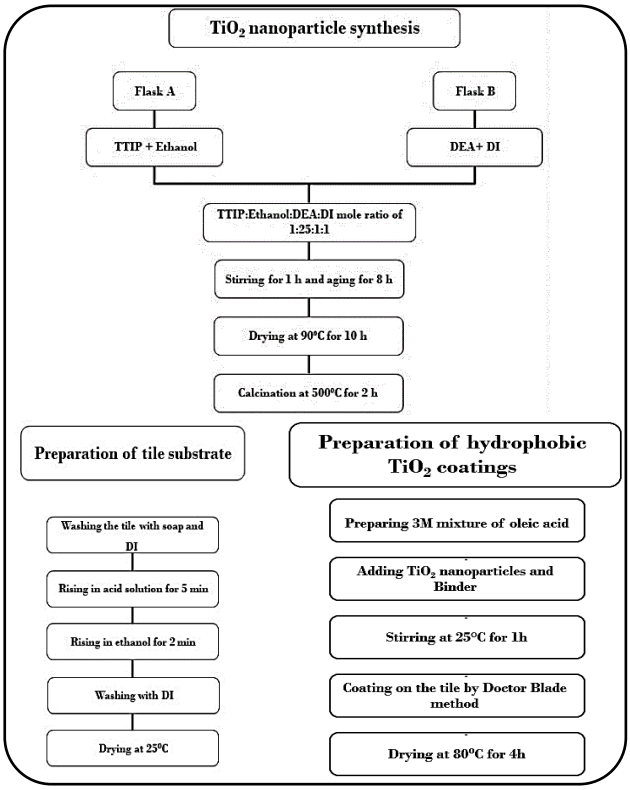

Fig. 1: Schematic flow chart for sol-gel synthesis of TiO_2 coatings and Hydrophobization of TiO_2 coatings.

EXPERIMENTAL SECTION

Materials

The reagents used in this study were Ethanol, titanium tetra isopropoxide, Diethanolamine (DEA), isopropanol, and oleic acid were obtained from Merck Company (Germany). Unsaturated polyester resin was supplied from (Changzhou Utek Composite Co.). Deionized water (DI) and *Escherichia Coli* bacteria (ATCC 25922) were obtained from Dr. Mojallali Company (Iran) and Bahar Afshan company (Iran), respectively. All the reagents were used without any further purification.

Nanophotocatalyst Preparation

Synthesis of TiO_2 nanoparticles

In order to synthesize TiO_2 nanoparticles, Titanium (IV) isopropoxide was first added dropwise to Ethanol in a molar ratio of 1:25 at 25°C under continuous stirring for 30 minutes. Then the Diethanolamine and deionized water in a ratio of 1:1 was added to the mixture under vigorous continuous stirring for 1 h and was aged for 8 h. The prepared sol was dried in an oven at 90°C for 10 h. Finally, TiO_2 xerogel was calcined at 500°C for 2 h.

Preparation of hydrophobic TiO_2 coatings

First, the tile substrate was washed twice with soap and water and then immersed in 3M hydrochloric acid solution for 5 min, in ethanol for 2 minutes, and finally washed with distilled water and dried at room temperature. In order to prepare the hydrophobic TiO_2 coatings, a 3M mixture of oleic acid, TiO_2 nanoparticles, and an organic binder in ethanol was prepared and stirred continuously at 25°C for 1h. Then the prepared sol was coated on the tile using the Doctor Blade method and dried at 80°C for 4 h.

Characterization of TiO_2 coatings

X-Ray Diffraction (XRD) analysis was used to investigate the crystal structure of the synthesized TiO_2 nanoparticles. To this aim, phase identification of hydrophobic TiO_2 photocatalyst was performed by XRD with the scanning rate of 0.05°/s using a Siemens D5000 diffractometer with Cu-Ka (λ= 1.54178 A°) radiation from 10° to 80°. The surface wettability and the contact angle of samplere determined by a contact angle measuring device. Fourier-Transform InfraRed (FT-IR) spectroscopy (BRUCKER, TENSOR27) was applied to determine functional groups and the FT-IR spectra was recorded from 4000 to 400 cm^{-1} at room 25°C. The surface morphology of the prepared hydrophobic coatings was characterized by scanning electron microscopy equipped with a field emission gun (FESEM, HITACHIS-109 4160). The antibacterial activity of the prepared coatings was studied in the degradation of methyl violet and *Escherichia coli* bacteria.

Experimental Setup

Photocatalytic activity of hydrophobic TiO_2 coatings was evaluated in photodegradation of Methylene Blue (MB), Methyl Orange (MO), And Congo Red (CR) under the UV light irradiation in a batch reactor on a magnetic stirrer. Experiments were carried out by locating 8 TiO_2 coatings (0.01 g TiO_2 per coating) on the bottom of the photoreactor for photodecomposition of 100 ml of dye solution under the two 6w UV lamps with a wavelength of 300–400w. The photocatalytic activity of TiO_2 coating was studied in the photodegradation of 10 ppm of mentioned dye solutions at 25°C and pH=7. For this purpose, 8 ceramic samples (7.6 cm×2.5 cm) coated with hydrophobic TiO_2 nanoparticles were positioned in the bottom of a glass container. The lamps were placed on top of the coatings at a distance of 5 cm. The changes in dye concentration were monitored by a UV-Vis spectrophotometer (Shimadzu1900i) at the maximum absorption wavelength of each dye during the photodegradation reaction. The photodecomposition efficiency of each dye is calculated by using the following equation:

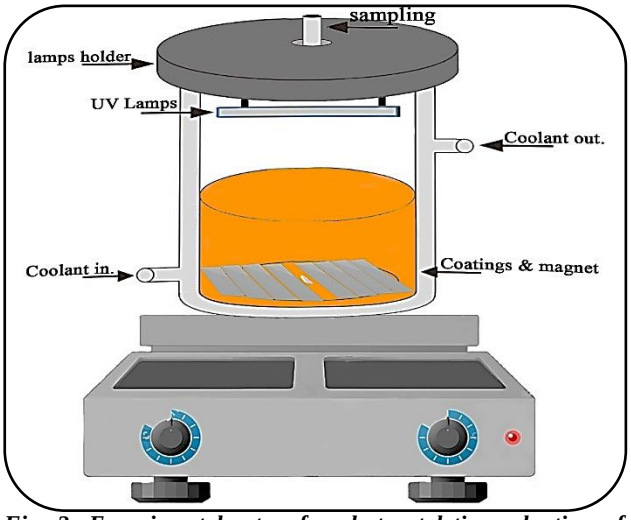

Fig. 2: Experimental setup for photocatalytic evaluation of TiO_2 coatings on glass plates in degradation of methylene blue

$$Degradation\ effiency\ \% = (1 - \frac{C}{C_0}) \times 100\% \qquad (1)$$

Which C_0 is the initial dye concentration, and C is the current dye concentration in the solution at specified times after irradiation.

RESULTS AND DISCUSSIONS

XRD Analysis of TiO_2 Coatings

The crystalline structure and crystals size has a significant effect on the antibacterial and photocatalytic activity of nanoparticles. The XRD pattern revealed a combination of rutile and anatase phases of TiO_2, and

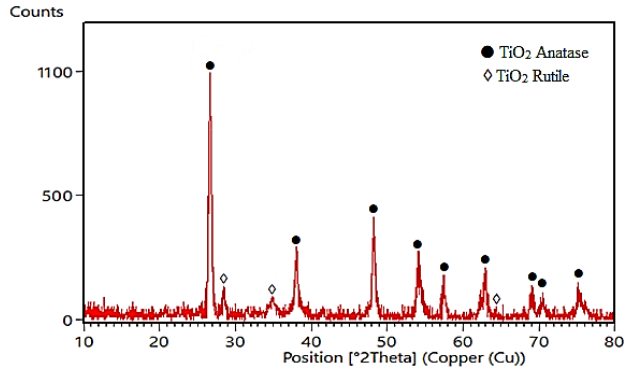

Fig. 3: XRD patterns of prepared hydrophobic TiO_2 coating

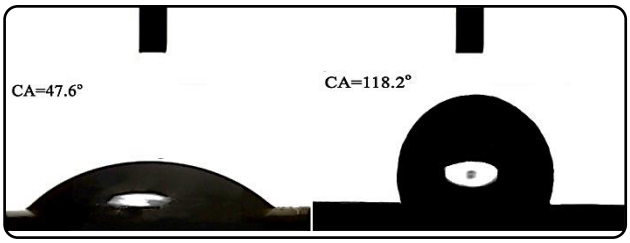

Fig. 4: Contact angle analysis of TiO_2 coatings before and after hydrophobization

the anatase phase has formed as the dominant phase. The reflections related to anatase were revealed in XRD pattern at 2θ values of 26.64º, 38.25º, 48.08º, 54.11º, 62.93º, 69.06º, 70.54º and 75.18º. These peaks can be attributed to lattice planes (101), (103), (004), (112), (200), (105), (211), (204), (116), (220), (215) and (224), respectively. The peaks formed at 2θ values of 27.58º, 35.32º and 64.41º indicate the rutile phase formation and are assigned to the lattice planes (110), (200) and (002), respectively. The XRD pattern of the synthesized TiO_2 nanoparticles agrees with the JCPDS Card no. 78-2486. The Scherer equation was used to specify the size of the formed crystals, and the average crystalline size was about 29 nm. In order to determine the mass fraction of rutile and anatase in the prepared hydrophobic TiO_2, the Spurr and Myers equation [24] used as follows:

$$A\ (\%) = 100/\{1+1.265(I_R\ /I_A)\} \quad (3)$$

$$R\ (\%) = 100- A\ (\%) \quad (4)$$

Where I_R and I_A represented intensities of the rutile (110) plane and anatase (101) plane, respectively. As calculated by this equation, the mass fraction of anatase and rutile were 85.4% and 14.59%, respectively.

Although the anatase phase has photocatalytic activity, the presence of a small amount of the rutile phase causes a rapid transfer of electrons to the conducting band and reduces the recombination rate.

Contact angle of TiO_2 Coatings

Contact angle analysis was used to evaluate the surface wettability and measure the contact angle between the water droplets and the coatings. Fig. 4 reveals the contact angle for each of the hydrophobic TiO_2 and hydrophilic TiO_2 coatings. As shown in Fig. 4, the contact angle for TiO_2 coatings without any surface modification is 47.60º. In contrast, the contact angle for hydrophobic TiO_2 nanoparticle coatings has been increased to 118.2º, which confirms the good effect of oleic acid in increasing the contact angle and reducing wettability. Increasing the contact angle and reducing the wettability level protects building surfaces, especially tiles, building facades, and concrete, and is very effectively reduces the growth of cracks, scaling of paint and gypsum surfaces, and the formation of mold and fungus[25].

FESEM Analysis of TiO_2 Coatings

Field Emission Scanning Electron Microscopy (FESEM) analysis was applied to evaluate the morphology of TiO_2 hydrophobic coatings on the tile substrate. Field Emission Scanning Electron Microscopy (FESEM) analysis was applied to evaluate the morphology of TiO_2 hydrophobic coatings on the tile substrate. According to Fig. 5, a uniform particle size distribution is observed without any agglomeration of nanoparticles and cracks on the coatings. The particles size distribution in the synthesized sample measured by ImageJ software and ranged between 29.7 and 87.5 nm. The small size of nanoparticles increases the number of atoms on the surface, increases the surface-to-volume ratio, reduces the penetration of pollutants, and reduces the mass transfer limits. Tiny nanoparticles have little light activity; therefore, to achieve quantum electrical and optical properties and limitation of the charge carriers' mobility, there is an optimal value for particle size to prevent the charge carriers' combination and their effects and increase the available surface area[18]. On the other hand, the lack of nanoparticles agglomeration and no cracks and holes in the synthesized sample reduces the electron-hole recombination and maximum adsorption of pollutants and photons by coatings[26]. It ultimately increases the antibacterial and photocatalytic activity of the prepared coatings.

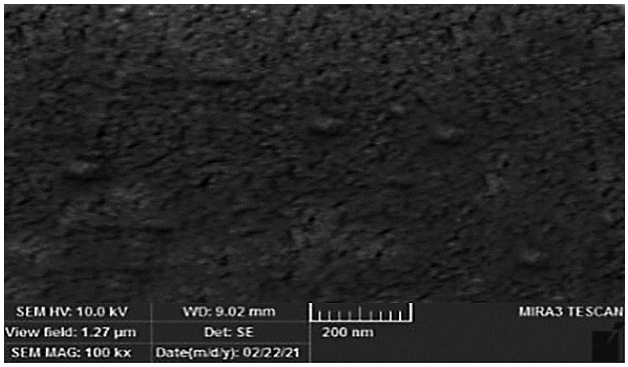

Fig. 5: FESEM up view image of hydrophobic TiO_2 coating

FT-IR analysis

FT-IR analysis was used to specify the functional groups in the synthesized nanoparticles. Fig. 6 shows the FT-IR pattern of surface-modified TiO_2 nanoparticles. Peaks observed between 800-500 cm^{-1} are related to the vibration of the Ti-O bonds [27]. The peaks observed between 1280-1640 cm^{-1} is attributed to the $–COO^-$ symmetric stretching and asymmetric stretching bonds. The appeared peak at 1710 cm^{-1} is assigned to stretching vibration of $-COOH^-$ group of oleic acid. Peaks in the range of 3080-2800 cm^{-1} are attributed to C-H bonds in the sample. The broad peak located at 3428 cm^{-1} is assigned to the stretching vibration of the hydroxyl groups (O-H).

Antibacterial activity of Surface-modified TiO2 coatings

The antibacterial activity of the manufactured hydrophobic TiO_2 coatings was studied in the inactivation of Gram-negative *Escherichia coli* bacteria by the disk diffusion method in Mueller Hinton Agar medium. According to the McFarland standard (1.5×10^8cfu/ml), the bacterial solution was cultured on a nutrient agar medium. For this purpose, 39 g of Mueller Hinton Agar powder was dissolved in deionized water and the medium was dispersed in plates after sterilization. Then, the bacteria were cultured isolatedly on Mueller Hinton medium and were incubated in an incubator (37ºC) for 24 h to grow [28, 29]. Then 1 ml of the bacterial sample was deposited on ceramic coated with hydrophobic TiO_2 nanoparticles and a normal ceramic sample as a control sample and incubated for 24 h at 37°C. The growth rate of the bacteria was evaluated after 18 h. The results of the experiments confirmed the lack of bacterial growth on the surface of the ceramic sample coated with TiO_2 nanoparticles; in the control sample, there was no evidence of *Escherichia coli* growth. The experiment was repeated three times. In the research conducted by *Ahmed et al*., acylated oligosaccharides (integrisides A and B) were used to deactivate *E. coli*. They reported the same results [6].

Sample	Bacteria	Irradiation	Zone of Inhibition (mm) (Diameter)			
			1	2	3	Mean
Hydrophobic TiO_2 coating	*E. Coli*	UV light	30	30	31	30.33
		Visible light	18	17	17	17.66
Tile without hydrophobic TiO_2 coating		UV light	0	0	0	0
		Visible light	0	0	0	

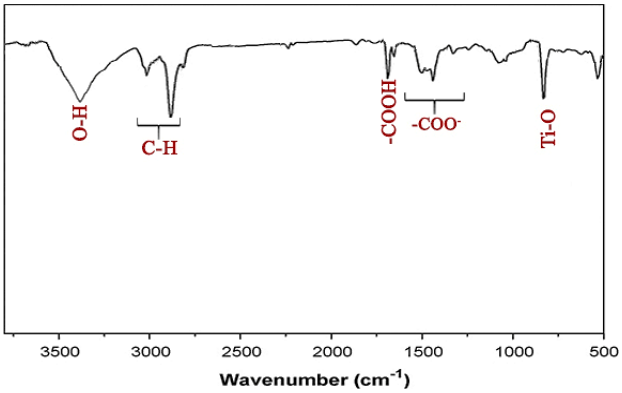

Fig. 6: FT-IR analysis of hydrophobic TiO_2 coating

Photocatalytic activity of TiO_2 and modified-surface TiO_2 coatings

The photocatalytic activity of TiO_2 coating was studied in the photodegradation of 10 ppm of various dye solutions at 25ºC and pH=7. At first the capability of TiO_2 and modified-surface TiO_2 coatings was studied in adsorption of MB, MO and CR in dark condition. According to Fig. 7, the adsorption of TiO_2 modified-surface coatings is higher than TiO_2 coatings. The results demonstrate that the adsorption of MB by the coatings is higher than compared to MO and CR. The MB adsorption by TiO_2 and modified-surface TiO_2 coatings are 33.1% and 29.93%, respectively. Fig. 8 reveals the photocatalytic activity of the coatings in the photodegradation of MB, MO, and CR. The results indicated that the coating has good photocatalytic activity in removing methylene blue, methyl orange, and Congo red. As depicted in Fig.7, the prepared hydrophobic TiO_2 coatings have degraded 94.57%, 81.33%, 73.66% MB, CR, and MO, respectively. As shown in Fig. 8, the photocatalytic degradation process has taken 150 min. The results revealed

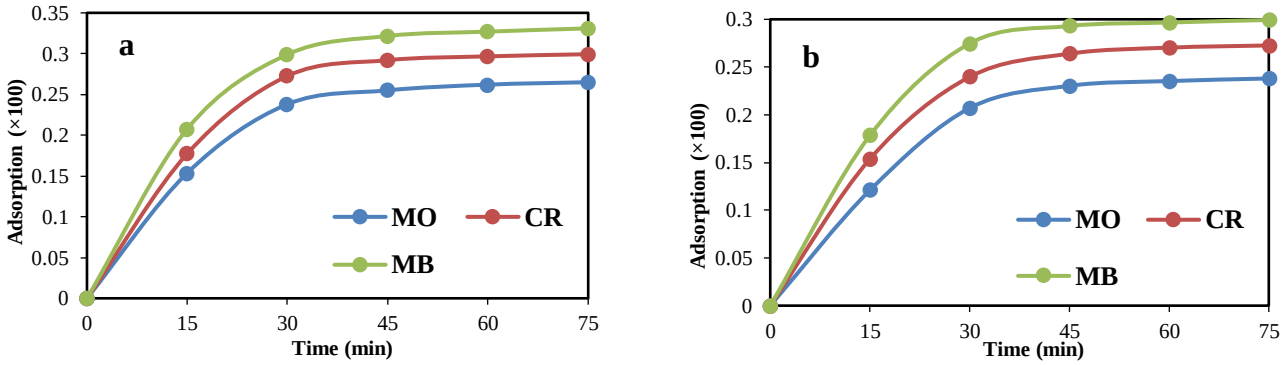

Fig. 7: (a) Adsorption of surface-modified TiO_2 coatings and (b) adsorption of TiO_2 coatings

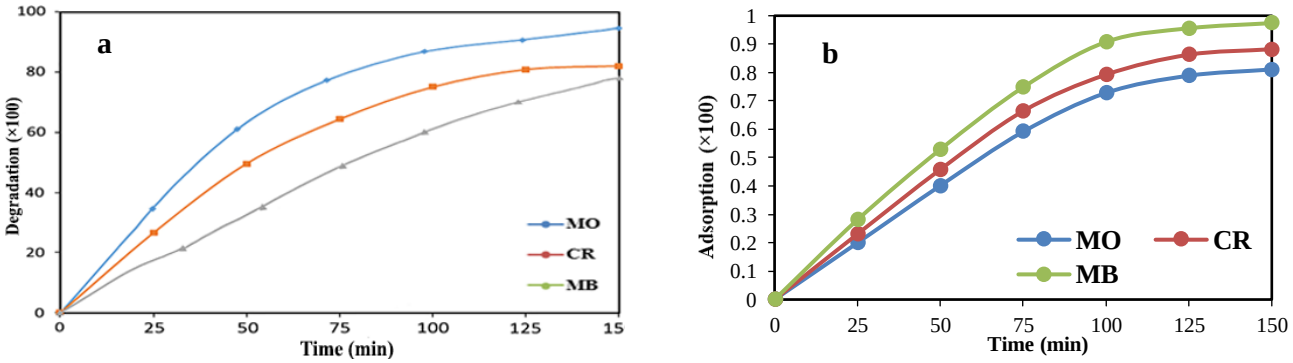

Fig. 8 (a) Photocatalytic activity of surface-modified TiO_2 coatings and (b) TiO_2 coatings

results revealed that the photocatalytic coatings had high photocatalytic activity in the decomposition of methylene blue compared to methyl orange and Congo red that can be related to the nature and chemical structure of the dyes. Other researchers also reported the same results [30, 31]. The wetting of the surface and contact angle between wastewater droplets and coatings affect the photodegradation efficiency [32]. The relationship between photocatalytic activity and contact angle can be investigated from two points of view. In hydrophilic surfaces, due to the better adsorption of hydroxyl radicals, the photocatalytic activity increases [33]. From another point of view, in hydrophobic and superhydrophobic surfaces, the adsorption of pollutants occurs better than in hydrophilic surfaces [34]. But in hydrophobic coatings, the adsorption of hydroxyl radicals and the contact between pollutants and photocatalytic coatings is better than in superhydrophobic coatings [31].

Durability and stability test of coatings

Salt spray test

The salt spray test was performed according to ASTM B1117 standard by neutral salt spray with 5% NaCl to evaluate the durability of coatings in corrosive environments. The TiO_2 hydrophobic coating with dimensions of 7 cm×15 cm was located in the salt spray machine with an angle of 30 degrees (Pars Ahrom, V300) at 37 °C for 24 h and 48 h periods. The pH of the saline solution was adjusted to 6.9. After each experiment, the sample was washed with distilled water and dried at 25 °C. The Shore D analysis and contact angle analysis were applied in order to study the durability and stability of the prepared hydrophobic coating. The Shore D hardness tester (Bareiss, Germany) and DIN 53505 standard were used for this purpose. The results of the Shore D test showed in Fig. 9. According to Fig. 9, no significant change was observed in the hardness resistance of the coating. The results of the Shore D test showed in Fig. 9. According to Fig. 9, no significant change was observed in the hardness resistance of the coating. As shown, the hardness resistance of the sample slightly decreased by increasing the time from 24 h to 48 h.

The contact angle analysis was applied to study the effect of salt spray corrosion on the hydrophobicity of the coatings. The results of contact angle analysis showed in Fig. 10. The results disclosed that by increasing the salt spray

Fig. 9. Shore D test of coating (A= fresh hydrophobic TiO_2 coating, B= after 24 h salt spray, C= after 48 h salt spray)

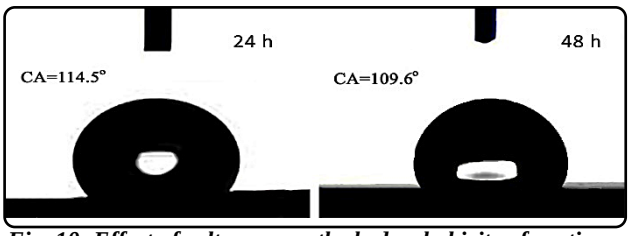

Fig. 10: Effect of salt spray on the hydrophobicity of coatings.

period, the hydrophobicity of samples slightly decreased. According to Fig. 10, by increasing the salt spraying time from 24 to 48 h, the contact angle of the coating has decreased from 114.5º to 109.6º.

Effect of ultrasound irradiation

To more study the adherence and durability of the coating, the sonication bath was used. To this end, the prepared coating was sonicated in an Ultrasonic bath with the 30 w ultrasound irradiation for 15 min in the pulse mode. This cycle was repeated 4 times. The sonicated coating after the sonication bath was dried at 90 °C for 8 h in the oven and weighed after cooling. According to the results, the prepared coating illustrated an excellent adherence to the substrate and high durability during the sonication process. The weight loss of coating was 0.005%. It seems the weight loss of coating during the ultrasonic bath is negligible.

Impact of pH on the degradation process

The surface charge of the photocatalyst must be neutral to take advantage of optimal photocatalytic activity and avoid an increase in the recombination rate. The performance of the photodegrading process was assessed at 3, 7, and 10 pHs to determine its effectiveness. Over 94.57% of methylene blue has decomposed at pH=7. In addition, degradation of methylene blue was 72.33% and 81.25% at pHs 3 and 10, respectively. At pHpzc, the photocatalysts' surface charge is neutral and depends on the photocatalyst's structure, known as the point of electric zero charge (pzc). Because pzc depends on the pH of the pollutant's solution, variations in pH affect the energy gap

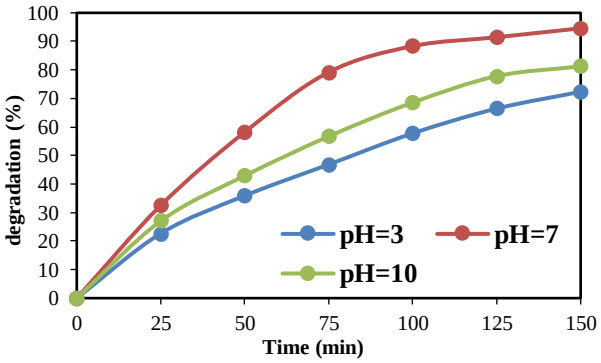

Fig. 11: Effect pH on photodegradation of methylene blue

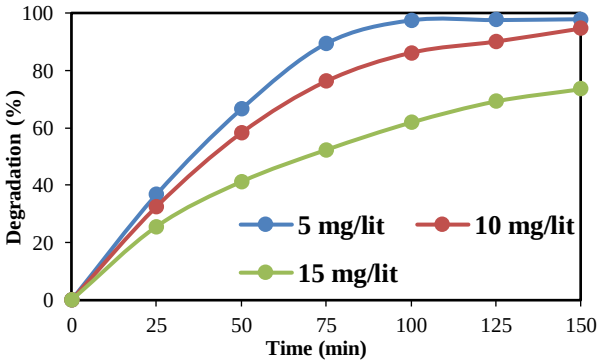

Fig. 12. Effect of initial dye concentration on photodegradation of methylene blue

potential and the semiconductor surface charge, which can prevent effective contact between dye molecules and the surface of photocatalyst. According to the results, the best pH for photodegradation of methylene blue over the prepared coatings was 7, and the photodegradation process had high efficiency at this pH.

Influence of different initial dye concentrations

In order to study the effect of dye concentration on degradation efficiency, methylene blue solutions were prepared with 5, 10, and 15 ppm. All experiments were carried out at pH=7 under irradiation of two 6w UV lamps. The results demonstrated that dye removal efficiency decreased by increasing the dye concentration. As shown in Fig. 12, the prepared coatings have decomposed 97.43% of 5 ppm initial dye concentration in 100 min. According to the results, 94.57% and 78.29% of 10 ppm and 15 ppm solutions of dye have degraded in 150 min, respectively. At high concentrations, due to the light scattering by dye molecules, fewer photons reach the surface of the photocatalyst, fewer hydroxyl radicals and electron-hole pairs are generated, and, consequently, photodegradation efficiency decreases.

CONCLUSIONS

TiO_2 nanoparticles were synthesized using the sol-gel method and coated by the Doctor Blade method on the tile as substrate. The surface of synthesized of TiO_2 nanoparticles was modified by oleic acid to increase the hydrophobicity of coatings. The contact angle test confirmed that oleic acid improved the hydrophobicity of TiO_2 coatings from 47.60º to 118.2º. XRD analysis revealed the good crystallinity of the prepared TiO_2 nanoparticles with both anatase and rutile phases. According to the FESEM analysis, the prepared hydrophobic coating was uniform and homogeneous without any cracks and holes on the surface. FESEM image demonstrated full coverage of the tile substrate. The prepared hydrophobic TiO_2 coatings had good antibacterial activity in the inactivation of *E. coli*. The photocatalytic activity of coatings was evaluated in the photodegradation of MB, MO, and CR. The results confirmed the high photocatalytic activity of TiO_2 and surface-modified TiO_2 coatings in the photodegradation of MB compared to MO and CR photodegradation. Salt spray test confirmed good stability and durability of hydrophobic TiO_2 coatings in corrosive environments. Shore D test and contact angle analysis revealed that by increasing salt spray time, hardness resistance and hydrophobicity of coatings slightly decreased.

Research Highlights

- Synthesis of TiO_2 nanoparticles via sol-gel method.
- Preparation of hydrophobic TiO_2 nanoparticles by oleic acid as surface modification agent and coating on the tile by using the Doctor Blade method.
- Study on the effect of oleic acid on contact angle of TiO_2 coatings.
- Photocatalytic degradation of various azo dyes (MB, CO, MO) using hydrophobic TiO2 coatings
- Study on the effect of operation parameters and salt solution on the durability of prepared hydrophobic TiO_2 coatings

Acknowledgements

The authors gratefully acknowledge Soran University as well as Urmia Nujan Nano fannavar company's complementary financial supports.

Received: Dec. 12, 2022 ; Accepted: Mar. 6, 2023

References

[1] Nsah K.T., "The Ecopolitics of Water Pollution and Disorderly Urbanization in Congo-Basin Plays", Orbis Litterarum (2021).

[2] Hosseinlou F., Environmental Ethics in Engineering Education: A Missing Link, *Majallah-i Amuzih-i Muhandisi-i Iran*, **22(88):** 91-105 (2021).

[3] Dewey H.M., Jones J.M., Keating M.R., Budhathoki-Uprety J., Increased Use of Disinfectants During the Covid-19 Pandemic and Its Potential Impacts on Health and Safety, *ACS Chemical Health & Safety***:** (2021).

[4] Hakki H.K., Allahyari S., Sonophotocatalytic Treatment of Wastewater Using Simulated Solar Light-Driven Bi_2O_3-ZnO Nanophotocatalyst Sensitized with Copper Phthalocyanine, *Materials Chemistry and Physics***:** 126355 (2022).

[5] Mahmood A., Khan S.U.-D., Rana U.A., Theoretical Designing of Novel Heterocyclic Azo Dyes for Dye Sensitized Solar Cells, *Journal of Computational Electronics*, **13(4):** 1033-1041 (2014).

[6] Irfan A., Sumrra S.H., Imran M., Assiri M.A., Khalid N., Al-Sehemi A.G., Quantum Chemical and Experimental Exploration of Biological Activity and Inhibitory Potential of New Acylated Oligosaccharides from Pistacia Integerrima Jl Stewart Ex Brandis, *Iranian Journal of Chemistry and Chemical Engineering (IJCCE)*, **40(5):** 1630-1641 (2021).

[7] Anil D.A., Aydin B.O., Demir Y., Turkmenoglu B., Design, Synthesis, Biological Evaluation and Molecular Docking Studies of Novel 1h-1, 2, 3-Triazole Derivatives as Potent Inhibitors of Carbonic Anhydrase, Acetylcholinesterase and Aldose Reductase, *Journal of Molecular Structure*, **1257:** 132613 (2022).

[8] Rose M., Christy R., Benitta T., Kumaran J., Bindhu M., Phase Transition in Zns Nanoparticles: Electrical, Thermal, Structural, Optical, Morphological, Antibacterial and Photocatalytic Properties, *Chalcogenide Letters*, **19(11):** (2022).

[9] Amiri M.R., Alavi M., Taran M., Kahrizi D., Antibacterial, Antifungal, Antiviral, and Photocatalytic Activities of TiO_2 Nanoparticles, Nanocomposites, and Bio-Nanocomposites: Recent Advances and Challenges, *Journal of Public Health Research*, **11(2):** 22799036221104151 (2022).

[10] Sarkın A.S., Ekren N., Sağlam Ş., A Review of Anti-Reflection and Self-Cleaning Coatings on Photovoltaic Panels, *Solar Energy*, **199:** 63-73 (2020).

[11] Najafidoust A., Hakki H.K., Avalzali H.A., Bonab M.K.A., The Role of Diethanolamine as Stabilizer in Controlling Morphology, Roughness and Photocatalytic Activity of Zno Coatings in Sonophotodegradation of Methylene Blue, *Materials Research Express*, **6(9):** 096401 (2019).

[12] Montazer M., Harifi T., "Antibacterial Nanocoatings", Elsevier, 399-413, (2020).

[13] Maury-Ramírez A., Flores-Colen I., Kanematsu H., "Advanced Coatings for Buildings, Multidisciplinary", Digital Publishing Institute, (2020).

[14] Maryani E., Nurjanah N., Hadisantoso E., Wijayanti R., "The Effect of TiO_2 Additives on the Antibacterial Properties (Escherichia Coli and Staphylococcus Aureus) of Glaze on Ceramic Tiles", IOP Publishing, 012011 (2020).

[15] Jeon Y., Nagappan S., Li X.-H., Lee J.-H., Shi L., Yuan S., Lee W.-K., Ha C.-S., Highly Transparent, Robust Hydrophobic, and Amphiphilic Organic–Inorganic Hybrid Coatings for Antifogging and Antibacterial Applications, *ACS Applied Materials & Interfaces*, **13(5):** 6615-6630 (2021).

[16] Law K.-Y., "Definitions for Hydrophilicity, Hydrophobicity, and Superhydrophobicity: Getting the Basics Right", ACS Publications, (2014).

[17] Hakki H.K., Allahyari S., Rahemi N., Tasbihi M., The Role of Thermal Annealing in Controlling Morphology, Crystal Structure and Adherence of Dip Coated TiO_2 Film on Glass and Its Photocatalytic Activity, *Materials Science in Semiconductor Processing*, **85:** 24-32 (2018).

[18] Hakki H.K., Allahyari S., Rahemi N., Tasbihi M., Surface Properties, Adherence, and Photocatalytic Activity of Sol–Gel Dip-Coated TiO_2–ZnO Films on Glass Plates, *Comptes Rendus Chimie*, **22(5):** 393-405 (2019).

[19] Akman E., Enhanced Photovoltaic Performance and Stability of Dye-Sensitized Solar Cells by Utilizing Manganese-Doped Zno Photoanode with Europium Compact Layer, *Journal of Molecular Liquids*, **317:** 114223 (2020).

[20] Kumar P.S., Sundaramurthy J., Zhang X., Mangalaraj D., Thavasi V., Ramakrishna S., Superhydrophobic and Antireflecting Behavior of Densely Packed and Size Controlled Zno Nanorods, *Journal of Alloys and Compounds*, **553:** 375-382 (2013).

[21] Najafidoust A., Asl E.A., Hakki H.K., Sarani M., Bananifard H., Sillanpaa M., Etemadi M., Sequential Impregnation and Sol-Gel Synthesis of Fe-ZnO over Hydrophobic Silica Aerogel as a Floating Photocatalyst with Highly Enhanced Photodecomposition of Btx Compounds from Water, *Solar Energy*, **225:** 344-356 (2021).

[22] Dargahi-Zaboli M., Sahraei E., Pourabbas B., Korgel B., One-Pot Synthesis of Hydrophobic Silica Nano Particles with Long-Chain Alcohol 1-Octadecanol**:**

[23] Gurav A.B., Latthe S.S., Vhatkar R.S., Lee J.-G., Kim D.-Y., Park J.-J., Yoon S.S., Superhydrophobic Surface Decorated with Vertical Zno Nanorods Modified by Stearic Acid, *Ceramics International*, **40(5):** 7151-7160 (2014).

[24] Spurr R.A., Myers H., Quantitative Analysis of Anatase-Rutile Mixtures with an X-Ray Diffractometer, *Analytical Chemistry*, **29(5):** 760-762 (1957).

[25] Alfieri I., Lorenzi A., Ranzenigo L., Lazzarini L., Predieri G., Lottici P.P., Synthesis and Characterization of Photocatalytic Hydrophobic Hybrid TiO_2-SiO_2 Coatings for Building Applications, *Building and Environment*, **111:** 72-79 (2017).

[26] Sarani M., Joshaghani A.B., Najafidoust A., Asl E.A., Hakki H.K., Bananifard H., Sillanpaa M., Sun-Light Driven Photo Degradation of Organic Dyes from Wastewater on Precipitation Ag_2CrO_4 over SiO_2-Aerogel and Nano Silica, *Inorganic Chemistry Communications*, **133:** 108877 (2021).

[27] Mahalingam T., Selvakumar C., Kumar E.R., Venkatachalam T., Structural, Optical, Morphological and Thermal Properties of TiO_2–Al and Tio2–Al2o3 Composite Powders by Ball Milling, *Physics Letters A*, **381 (21):** 1815-1819 (2017).

[28] Pormohammad A., Nasiri M.J., Azimi T., Prevalence of Antibiotic Resistance in Escherichia Coli Strains Simultaneously Isolated from Humans, Animals, Food, and the Environment: A Systematic Review and Meta-Analysis, *Infection and Drug Resistance*, **12:** 1181 (2019).

[29] Singh G., Joyce E.M., Beddow J., Mason T.J., Evaluation of Antibacterial Activity of Zno Nanoparticles Coated Sonochemically onto Textile Fabrics, *Journal of Microbiology, Biotechnology and Food Sciences,* **2(1):** 106-120 (2012).

[30] Liu J., Ye L., Wooh S., Kappl M., Steffen W., Butt H.-J.r., Optimizing Hydrophobicity and Photocatalytic Activity of Pdms-Coated Titanium Dioxide, *ACS Applied Materials & Interfaces,* **11(30):** 27422-27425 (2019).

[31] Ghashghaee M., Fallah M., Rabiee A., Superhydrophobic Nanocomposite Coatings of Poly (Methyl Methacrylate) and Stearic Acid Grafted Cuo Nanoparticles with Photocatalytic Activity, *Progress in Organic Coatings,* **136:** 105270 (2019).

[32] Wang X., Ding H., Sun S., Zhang H., Zhou R., Li Y., Liang Y., Wang J., Preparation of a Temperature-Sensitive Superhydrophobic Self-Cleaning SiO_2-TiO_2@ Pdms Coating with Photocatalytic Activity, *Surface and Coatings Technology,* **408:** 126853 (2021).

[33] Schwarz P.F., Turro N.J., Bossmann S.H., Braun A.M., Wahab A.-M.A.A., Duerr H., A New Method to Determine the Generation of Hydroxyl Radicals in Illuminated TiO_2 Suspensions, *The Journal of Physical Chemistry B,* **101(36):** 7127-7134 (1997).

[34] Guan K., Relationship between Photocatalytic Activity, Hydrophilicity and Self-Cleaning Effect of TiO_2/SiO_2 Films, *Surface and Coatings Technology,* **191(2-3):** 155-160 (2005).