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## **Original Research Article**

## Evaluation of Thermal Stability of TiO<sub>2</sub> Applied on the Surface of a Ceramic Tile to Eliminate Methylene Blue Using Silicabased Doping Materials

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## ABSTRACT

Nanotechnology is a promising and practical method for removing volatile organic materials from tile surfaces. Tiles are usually coated at temperatures above 1000 °C. At temperatures above 500 °C, TiO<sub>2</sub> cannot maintain its photocatalytic properties due to the anatase to rutile phase transformation, making it difficult to perform the method. One of the main goals of this study is to explore the possibility of producing TiO2 nanostructures through a simple and cost-effective method without requiring any modifications to existing factory production lines. In this experimental study, the nanostructure of TiO2 was doped with nickel and nitrogen ions, prepared based on silica through the sol-gel method, and mixed with a glaze called nanoglaze. The resulting nanostructure was calcined at 1200 °C, where the molecular ratio of silica-based doped TiO2 was changed. The nanoglaze was coated on the blocks and placed under the CFL lamp. SEM, FTIR, XRD, and TGA techniques were used to analyze its nanostructure. The results showed the thermal stability of the nanostructure at 1200 °C. TiO<sub>2</sub> shows a photocatalytic effect only in the ultraviolet region. The removal rate of Methylene Blue as a pollutant sample was tested. The removal rate of methylene blue was 44% in the presence of titanium dioxide photocatalyst. According to XRD analysis, the size of the photocatalyst crystal particles was 3.5 nm. Adding TiO<sub>2</sub> removes pollutants from water and air. Also, self-cleaning properties appear in these materials. So, photocatalysts can be added to building structures, pavements, paints, cement and plaster.



#### Introduction

The advanced oxidation process is a new technique for removing pollution by semiconductor catalysts. Light radiation creates electron holes in the structure of the semiconductor [1,2]. The electrons and holes produced cause water to hydrolyze and produce radical assemblies. Radical assemblies destroy pollution, and this process is known as photo composition. Titanium dioxide is attractive to researchers because of its semiconducting properties and the ability to remove environmental pollutions such as nitrogen oxides, volatile organic compounds (VOCs), and bacteria, as well as metal protection and anti-fog characteristics [3]. One of the characteristics of titanium oxide is its three phases of anatase brookite - rutile. The anatase phase is particularly interesting for its photocatalytic

properties because it functions better than the other two phases [4]. The anatase phase has a better charge, and its surface hydroxyl has a higher specific gravity. The advantages of  $TiO_2$  are its non-chemical, non-toxic nature and inexpensiveness. The catalytic activities of titanium oxide are determined by its crystal structure's chemical and physical properties, particle size, surface area, and so on. Several effective parameters are considered to improve and optimize the catalytic activity of titanium dioxide for the isolation of volatile materials: 1. Surface area 2. Prevention of recombination of electrons and holes 3. Type of titanium oxide phase [5].

In general,  $TiO_2$  is stimulated by ultraviolet (UV) light with a wavelength of  $\geq$ 387 nm, which is 3 to 5% of the solar spectrum. Therefore, it involves a small quantum yield (3.2 *EV*) limited by the gap band and has poor photocatalytic efficiency [6]. Photocatalytic interactions are reversible, and the holes and electrons recombine very quickly. To solve these problems, the doping method has been developed to optimize the efficiency of titanium dioxide [7]. The advantages of titanium dioxide doped with metallic and non-metallic ions include: First, doping reduces the gap band energy. Second, doping stabilizes the anatase phase at high temperatures and delays the anatase to rutile phase transformation.

As stated above, doping enhances the stability the photocatalytic titanium dioxide at of temperatures above 450 °C and prevents the anatase to rutile phase transformation [8]. As a result, better and higher photocatalytic activities take place. In some conditions, titanium dioxide can be used as a photocatalyst to produce building materials such as cement blocks, roof blocks, and glass, produced at 650-1200 °C. By changing the composition of TiO<sub>2</sub>, a phase change occurs at high temperatures, and self-cleaning building materials can be produced without fundamental changes in the production line [9]. Two methods have been considered to stabilize the anatase phase of  $TiO_{2}$ , including 1. Doping 2. Using silica as a catalytic base. The advantage of doping is that under visible light, it prevents electron-hole recombination [10]. The supporter (catalytic base) increases the catalyst's surface area and the polluted molecules' adsorption rate, eliminating volatile organic matter.

Indoor air pollutants comprise nitrogen oxides, volatile organic compounds, and other particles. These pollutants originate from various sources, including combustion, construction materials, and used products. Many volatile organic compounds are known to be toxic and carcinogenic. Photocatalytic oxidation presents an effective option for improving indoor air quality for two reasons. Firstly, it can convert many organic pollutants into harmless inorganic compounds like CO<sub>2</sub> and H<sub>2</sub>O. Secondly, indoor environments generally have low pollutant concentrations, allowing the photocatalytic

decontamination process to be effective over an extended period. Photocatalysts are often incorporated into building materials and products intended for air purification in indoor environments.

Harino *et al.* synthesized TiOSO4 and tetraethyl orthosilicate solutions using hydrolysis under hydrothermal Titania, which had thermal stability up to 1300 °C. However, the method of synthesizing and stabilizing titanium dioxide proposed by Harino *et al.* was costly and timeconsuming [11]. Hong Zhang *et al.* doped commercial titanium dioxide with nickel in various proportions. Then they calcined the resulting material at 350 °C. They reported the best value for doping nickel at 2% mol. The authors also reported that the crystallinity decreases as the doping level increases [12].

In 2018, Shi *et al.* obtained thermal stability up to 1000 °C by synthesizing TiOF<sub>2</sub>. Unfortunately, this method induced anatase to rutile phase transformation at a temperature of 1200 °C. Other disadvantages of the method used by Si include that the highest photocatalytic activity is obtained at a temperature of 500 °C, and it decreases sharply with increasing temperature, although no phase change occurs. Also, the Si method can only degrade acetone [13].

In 2019, Bedilo *et al.* studied the thermal stability of  $TiO_2$ . Their results indicated that doping could increase thermal stability. The highest thermal stability temperature created when using the doping method was 600 °C, in which only 64% of the  $TiO_2$  formed the anatase phase [14].

Most recently, Bedilo *et al.* could achieve thermal stability up to 800 °C by synthesizing  $TiO_2$  using the silica catalytic base. The authors reported that the anatase phase stability was induced only up to 1000 °C [15].

The main objective of the current experimental study is to maintain the stability of doped TiO2 with photocatalytic properties at temperatures above 1000 °C and to investigate its cleaning

abilities. Thus, TiO<sub>2</sub> nanostructures on a silica base are doped with nickel and nitrogen ions using a simple and economical method. One of the additional goals of this study is to explore the possibility of producing TiO<sub>2</sub> nanostructures through a simple and cost-effective approach without requiring any modifications to existing factory production lines. For this purpose, in a comprehensive study, the stability of the silicabased nano photocatalyst structure will be investigated using co-doping of nickel and nitrogen ions at temperatures above 1000 °C. Techniques such as SEM, XRD, FTIR, and TGA are used for nanostructure analysis. It is expected that with the use of dopant and silica, the anatase to rutile phase transformation at high temperatures will be delayed, which is very important for some industrial applications, including self-cleaning, when used in surface coating. It also preserves the environment because it lacks chemical detergents [13].

## **Experimental Details**

#### Materials

Table 1 lists the chemicals used and their sources. The conditions under which the experiments were performed are as follows: For the co-doping of titanium dioxide, 0.24 moles of nitrogen and 0.00099 moles of nickel was used. In addition, silica was added as a base with various proportions  $Ti / Si = \frac{36}{64}$ ,  $\frac{27}{73}$ ,  $\frac{45}{55}$  to the co-doping. The resulting mixture was calcined at 550 to 1200 °C [16].

To prepare the solvent of the coating material, 0.1 g of photocatalyst powder was mixed with tile glaze and coated on the tile with the dimensions of  $5 \times 1 \times 5$ .

Material	Chemical formula	Company
Titanium tetra isopropoxide	$C_{12}H_{28}O_4Ti$	MERCK
Tetraethyl orthosilicate	$SiC_8H_{20}O_4$	MERCK
Nitric acid	HNO <sub>3</sub>	MERCK
Ethanol	$C_2H_6O$	MERCK
Nickel Nitrate	Ni(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O	MERCK
Urea	$CH_4N_2O$	MERCK
Ethyl acetate	$C_4H_8O_2$	Titrachem

Table 1. Chemicals	used for	experiments
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#### Photoreactor and pollution reduction assessment

With a purity of 99.9%, titanium dioxide, nickel nitrate, silicon dioxide, and urea were purchased from Merck, Germany. For the two-component doping process of  $TiO_2$ , nickel nitrate and urea were added to 100 mL of deionized water containing  $TiO_2$ . It is important to note that nickel nitrate supplied the required nickel, while urea provided the necessary nitrogen. The mixture

was then stirred for two hours using a magnetic stirrer (IKA ICT, Germany) and placed in an ultrasonic device (Hielscher, Germany) for one hour. Finally, the resulting mixture was placed on a heater at a temperature of 100 °C, allowing the solvent to evaporate and yielding the doped titanium dioxide in powder form. Figure 1 reveals the schematics of the processes in which the experiments were performed as follows:



Figure 1. Schematic of catalyst synthesis process

To study the oxidation of MB with the presence of Nanoglaze film, a glass cylinder with a length of 4 cm, an inner diameter of 5 cm, and a volume of 0.087 liters was placed on a tile with dimensions of 5 x 5 x 1 cm. The tile was washed with ethanol and then distilled water to remove all existing pollutants. Finally, the tile was placed inside the oven. After removing from the oven, 15 mL (55 ppm) of MB solution was poured on the tile [16,17]. The adsorbed material was

measured using an uncoated tile as a reference and by applying the UV-vis spectrophotometer at the wavelength of 664 ppm. In the second stage, the CFL lamp light was radiated on the tile for four hours. The distance between the lamp (CFL-50w) and the tile was 13 cm [17]. Visible light was amplified to 4000 x 10 Lux, and at a distance of 13 cm, it was 1700 x 10 Lux. Figure 2A demonstrates the experimental setup, and Figure 2B reveals an example of a coated tile.



Figure 2. (A): A sample of coated tile, (B): A schematic of the prepared reactor.

After pouring the solution into the glass reactor, the reactor was immediately placed in the dark for 3 h to confirm the oxidation process. The MB was then measured, and the spectrophotometric test was performed on the sample again [16]. The percentage reduction of pollution was calculated by Equation 1.

MB decolorization (%) = 
$$\frac{A_0 - A}{A_0} * 100$$
 (1)

 $A_0$  and A show the pollution absorption rate before and after oxidation.

#### Identification of modified catalyst

#### XRD (X-ray diffraction)

To determine the crystal structure of the synthesized particles as well as the size of the crystals and the material phase the XRD device (SIEMENS D5000) was used. The size of the crystals was estimated using Equation 2:

$$D = K\lambda / \beta \cos \theta \tag{2}$$

Where D represents the crystal size of the sample, K is a constant number,  $\lambda = 1542$  nm is the radiant wavelength of the diffractometer,  $\beta$  the amplitude at half the height of the highest peak, and  $\theta$  the Bragg angle [18].

## FT-IR (Fourier-transform infrared spectroscopy)

Using the FTIR technique, someone can identify chemical bonds, molecular interactions, and especially the functional groups of materials by studying the device's output infrared spectrum. The FT-IR device used in the current study was TENSOR 27 (Germany, Brucker). Samples were collected using a Bruker Equinox 55 Spectrometer as diluents in the wavenumber range 4000-400 cm<sup>-1</sup>, using 15 scans per sample [19].

## SEM (Scanning electron microscope)

SEM analysis (LEO44oi England), one of the most widely standard microscopic analysis methods, was used to examine the catalyst's morphology, the structure's size, and the distribution of the particles in the synthesized material. The utilized device was equipped with energy dispersion spectroscopy (EDS–EDX) and a detector (Bruker AXS, software: Quantax) [20].

## Thermal gravimetric analysis (TG-DTA)

Thermal gravimetric analysis (TG-DTA) of the samples was carried out using an appropriate device (DTA-TG SDT Q600 V20.9 Build 20) in air flow with a heating rate of 10 °C/min in the temperature range of 25-1000 °C

## **Results and discussion**

Structural study

Figure 3A depicts the XRD spectrum of crystalline TiO<sub>2</sub> material calcined at 550 °C. In Figure 3, the peak observed at  $2\theta \sim 25.5^{\circ}$  corresponds to the anatase phase's crystal plate (101). The other peaks observed for the anatase phase are at ~38°, 48°, 54°, 55°, and 63° corresponding to the crystal plate (004), (200), (105), (211), and (204), respectively. These data follow the card (JCPDS Card no. 21-1272).

Figure 3B shows the synthesized N:Ni:TiO2 XRD pattern at 550 °C. It can be observed that the simultaneous doping of TiO<sub>2</sub> with the non-metal (nitrogen) and metal (nickel) causes the structure to become amorphous and the peak of the anatase phase index of TiO<sub>2</sub> to appear wider [14,21]. It was also shown that nitrogen and nickel precursors did not significantly affect the crystalline phase of the anatase peak. Figure 3C depicts the XRD pattern of N:Ni:TiO<sub>2</sub> deposited on the silicate substrate. As seen in Figure 3, the deposition of the material on the silicate substrate has caused the silica peak to appear wide at  $2\theta$  at ~20°. The peak corresponding to the anatase phase of  $TiO_2$  has possibly appeared on the right (side) of the silica peak, but it is not visible in this figure due to its lower intensity compared to the silica peak. In Fig. 3D, N:Ni:TiO<sub>2</sub> is calcined and deposited on the silica substrate at 650 °C after increasing the temperature by 110 °C. This causes the silica and  $TiO_2$  peaks to be seen in proximity [22]. The reason for this is the change in the ratio of the anatase phase to the rutile phase due to increasing temperature.

In Figure 3E, N: Ni:TiO<sub>2</sub> was calcined and deposited on a silica substrate at 750 °C after increasing the temperature by 190 °C. In Figure 3F, N:Ni:TiO<sub>2</sub> was calcined and deposited on a silicate substrate at 850 °C after increasing the temperature by 100 °C. It is observed that the increase in temperature in these two figures increases the peak intensity of the rutile phase compared to silica and further separation of the peaks, which is due to the intense activity of the anatase phase of TiO<sub>2</sub> compared to silica [15].



**Figure 3.** XRD patterns of A) synthesized TiO<sub>2</sub> calcined at 550 °C, B) synthesized N:Ni:TiO<sub>2</sub> calcined at 550 °C, C) synthesized N:Ni:TiO<sub>2</sub>/SiO<sub>2</sub> calcined at 550 °C, D) synthesized N:Ni:TiO<sub>2</sub>/SiO<sub>2</sub> calcined at 650 °C, E) synthesized N:Ni:TiO<sub>2</sub>/SiO<sub>2</sub> calcined at 750 °C, F) synthesized N:Ni:TiO<sub>2</sub>/SiO<sub>2</sub> calcined at 850 °C, J) synthesized N:Ni:TiO<sub>2</sub>/SiO<sub>2</sub> calcined at 1100 °C, H)synthesized N:Ni:TiO<sub>2</sub>/SiO<sub>2</sub> calcined at 1200 °C. The tallest peak in circles on figures is for the TiO<sub>2</sub> anatase phase

Figure 3G shows the spectrum of N:Ni:TiO<sub>2</sub> calcined at 1100 °C and deposited on a silicate substrate. Finally, Figure 2H shows the N:Ni:TiO<sub>2</sub> spectrum calcined at 1200 °C and deposited on a silicate substrate. It should be noted that, in the anatase phase,  $2\theta$ =21.2 for silica and  $2\theta$ =25 for titanium dioxide. However, due to the overlap,

the two cannot be distinguished. If the phase of titanium dioxide has been changed to rutile, a peak should be observed at  $2\theta$ =28 with an intensity of about 400 (a.u.). No phase change has occurred since no peaks are observed in this region [23].

#### FT-IR analysis

Figure 4A is the spectrum of the most optimal co-doped photocatalyst  $N:Ni:TiO_2$  without silica base and calcined at 80 °C. The peaks between the wavelengths of 400-1000 cm (1 cm) are related to the vibration of the Ti-O and Ti-O-Ti bonds. The peaks at 1300 cm (cm<sup>-1</sup>) and 1026 (cm<sup>-1</sup>) correspond to the peaks of nickel and

nitrogen ions in the photocatalyst structure, which are indistinguishable. The peak in the region 3000-3500 (cm<sup>-1</sup>) belongs to the titaniumbonded hydroxyl group (OH-Ti) [24]. Overall, the results obtained from the FT-IR spectrum show that the catalysts have been synthesized correctly and confirm that doped materials are present in the structure.



**Figure 4.** Surface hydroxyl groups and the chemical interaction of A) the amorphous TiO<sub>2</sub> dried at 80 °C, B) the N:Ni:TiO<sub>2</sub> (E) calcined at 550 °C, and C) the N:Ni:TiO<sub>2</sub>/SiO<sub>2</sub> calcined at 1100 °C

Figure 4B presents the spectrum of the most optimal co-doped photocatalyst N:Ni:TiO<sub>2</sub> without silica base, calcined at 550 °C. The peaks are related to the 400-1000 (cm-1) wavelengths Ti-O and Ti-O-Ti bond vibrations. The 1020 and 1238 (cm<sup>-1</sup>) peaks are related to nickel and nitrogen ions in the photocatalyst structure [14,15]. The peak in the region 3010-3500 (cm<sup>-1</sup>) belongs to the intramolecular bond of the hydroxyl group with OH-Ti, and the peaks at the wavelength 2850 and 2918 (cm<sup>-1</sup>) belong to C-H. The reason for this is the calcification of C-H at

550°C and the burning of the photocatalyst. The figure indicates the prominent peaks of the doping material.

Figure 4C shows the silica-based co-doping of N:Ni:TiO<sub>2</sub>/SiO<sub>2</sub> calcined at 1200 °C, which shows a molecular weight of Ti/Si=44/55. The obtained spectrum absorption is based on %Transmittance and wavelength ranging from 400 to 4000 (cm<sup>-1</sup>). The peaks in the wavelength ranging from 400-1000 (cm<sup>-1</sup>) are related to the vibration of Ti-O and Ti-O-Ti molecules. The peak in the region 3010-3500 (cm<sup>-1</sup>) is related to the physical absorption of water, and the chemical absorption of water occurs when the OH-Ti peak is determined in the range 3200-3400 (cm<sup>-1</sup>) [25]. The peak in the range 1600 (cm<sup>-1</sup>) is related to the physical absorption of water on the TiO<sub>2</sub> surface.

In Figure 4C, two new peaks at wavelengths 970 and 1070 (cm-1) indicate the photocatalyst structure's chemical adsorption. The peak observed at wavelength 970 (cm<sup>-1</sup>) is related to the Ti-O-Si and Si-O bonds. Also, the peak in the wavelength 1070 (cm<sup>-1</sup>) is related to the Si-O-Si bond, which is amorphous and has formed due to the non-reaction of silicon with titanium. The peak at 1072 (cm<sup>-1</sup>) is the structure of the Ti-O-Si photocatalyst related to the combination of Titania and silica base, which has a higher photocatalytic activity than TiO<sub>2</sub> [13, 25]. One of the reasons for this is the formation of Lewis (electron pair acceptor) and Bronsted (proton donor) acidic sites.

# Morphological studies (SEM-Scanning Electron Microscopy)

Scanning electron microscopy was used to observe the morphology of co-doped silica-based titanium dioxide. Figure 5 shows SEM images of N:Ni:TiO<sub>2</sub>/SiO<sub>2</sub> calcined at 550, 650, 750, 850 °C, 1100 °C, and 1200 °C. Figures 5A and 5B show the investigated surface with low magnification. As the magnification increases, an irregular morphology is revealed [12,20]. Besides, a large density of nanoparticles can be observed. As can be seen, most particles stack together in spheres with increasing temperature. Note that the distribution of the particles is uniform. However, a few particles join together, appearing as lumps in a sphere shape [26]. According to Figures 5C and 5E (reduced magnification), the sample is characterized by a flat surface. These results indicate the combination of titanium dioxide and silica. A small unit of titanium dioxide is first formed in the hydrophilic area of the copolymers. With the continuation of the reaction, silica units are formed around the titanium dioxide particles, and the titanium dioxide particles are deposited on the surface of the porous walls [27].

Figures 5D and 5F depict SEM images with a magnification of 500 nm. As is apparent, an irregular morphology can be seen as the magnification increases. Of course, a small number of agglomerated particles could also be observed. It should be noted that the composite is heterogeneous due to the heat generated. In addition, small cavities and lines on the particles are a sign of loss of organic components during the calcination process. This type of morphology improves photocatalytic activity, surface area, and photocatalyst characteristics. In addition, it is clear from these images that the particles are heterogeneously distributed and also that most particles are densely packed [17,18].

In Figure 5G, an SEM image of N: Ni:TiO<sub>2</sub>/SiO<sub>2</sub> calcined at 1100 °C is presented at 500 nm magnification, displaying the length of the holes. The presence of such cavities, as explained earlier, indicates a morphology conducive to enhanced photocatalytic activity, thereby improving the characteristics of the photocatalyst.

Figure 5H, the SEM image of N:  $Ni:TiO_2/SiO_2$  calcined at 1200 °C is captured at a magnification of 200 nm, revealing an irregular morphology. As evident from the image, several particles are aggregated together. The heterogeneous

appearance of the composite is likely due to the heat generated during the process. Additionally, the letter 'D' in the figure indicates the diameter of the particles. From images 5G and 5H, it can be observed that spherical nanoparticles have accumulated over the entire surface. Particles that can be recognized at the nanometer scale are primary and are accumulated to produce secondary particles with larger dimensions [28].



**Figure 5.** SEM morphology of A) synthesized bare  $TiO_2$  calcined at 550 °C, B) synthesized N:Ni: $TiO_2$  calcined at 550 °C, C) synthesized N:Ni: $TiO_2/SiO_2$  calcined at 550 °C, D) synthesized N:Ni: $TiO_2/SiO_2$  calcined at 650 °C, E) synthesized N:Ni: $TiO_2/SiO_2$  calcined at 750 °C, F) synthesized N:Ni: $TiO_2/SiO_2$  calcined at 850 °C, G) synthesized N:Ni: $TiO_2/SiO_2$  calcined at 1100 °C, H) synthesized N:Ni: $TiO_2/SiO_2$  calcined at 1200 °C

The particle size of N:Ni:TiO<sub>2</sub>/SiO<sub>2</sub> calcined at 1100 °C is 10 to 30 nm, and the particle size distribution range is relatively narrow. Also, the particle size of N:Ni:TiO<sub>2</sub>/SiO<sub>2</sub>, which is calcined at 1200 °C, is in the range of 90 to 120 nm, and the particle size distribution has increased compared to 1100 °C. It can be said that relatively larger particles were observed with increasing temperature. In the calcined sample at 1200 °C, it is observed that the solid surface is more uniform compared to the calcined sample at 1100 °C [20,28].

#### Photocatalytic degradation

To investigate the pollution reduction through photocatalytic oxidation, the photocatalytic activity of co-doped silica-based titanium dioxide investigated using methylene was blue degradation, which is considered an organic substance [19]. 55 ppm of the methylene blue solution was poured from a glass cylinder on the tile (reactor), and the UV lamp was placed at a distance of 13cm from the sample. Α spectrophotometer was used to evaluate the effect of decontamination. Methylene blue degradation test was performed on two types of tiles: 1. Glazed tiles 2. Unglazed tiles. After obtaining the MB adsorption rate in these two cases, the decontamination percentage was

calculated using the equation of decontamination

percentage = 
$$\frac{A_o - A}{A_o} \times 100$$
, where  $A_0$  indicates

contamination absorption without photocatalyst and *A* the contamination absorption with catalyst [24, 25].

Figure 6A indicates an example showing silicabased doped titanium dioxide with a molar ratio of 44 to 55. Also, in Figure 6A, sample 2 shows a molar ratio of 27 to 37, and sample 3 illustrates a molar ratio of 36 to 64. After calcination of silicabased doped titanium dioxide at 750 °C, sample 1 was selected as the best photocatalyst with the highest degradation rate of the organic matter. In exposure to visible light for 4 h, 44% of methylene blue was degraded [28].

Figure 6B shows the results of methylene blue degradation. The figure shows the spectrum of MB absorption by composite A (under CFL irradiation), composite B at 750 °C, composite C at 850 °C, composite D at 1100 °C, and composite E at 1200 °C. Figure B6 shows the decrease in MB concentration after 3 h under CFL irradiation. This is due to the self-cleaning characteristic of titanium dioxide, which is doped with nickel and nitrogen ions and reduces the gap band. Nickel and nitrogen ions reduce the crystalline size of titanium dioxide and increase the surface area, thus improving photocatalytic performance [28,29].



Figure 6. Methylene blue degradation for different samples

#### TGA analysis

The results of TGA analysis (Germany, model TA, Q600) related to the N:Ni:TiO<sub>2</sub>/SiO<sub>2</sub> photocatalyst with a molar ratio of 1:1 are presented in Figure 7. As can be seen in the figure, 1.8% of the weight of the photocatalyst has decreased in three stages. The weight loss up to 250 °C is related to the loss of water and alcohol in the photocatalyst structure [30-35]. In the second stage, the weight loss is related to the burning of organic materials and the destruction of hydroxyl groups, resulting in the formation of photocatalysts. In the third stage, the weight loss is due to the change of the structure of the

photocatalyst from amorphous to crystalline state, but the phase change of anatase to rutile has not happened. It is necessary to explain that no peak can be seen in Figure 7. If a peak is observed, it is assumed that the phase changes from anatase to rutile. The analysis was taken up to a temperature of 1000 °C, which agrees with the X-ray diffraction results [36]. The point worth mentioning in the thermal analysis curve is that considering that this analysis was done in an environment containing argon (50%) and air (50%), the increasing trend observed after the temperature of 450 °C is due to the sample reacts with air [37]. Note that the initial weight of the sample used in the analysis was 3.557 mg.



Figure 7. Thermal analysis of silica-based titanium dioxide photocatalyst up to 1000 °C

## Conclusions

Photocatalytic oxidation is one of the methods used to degrade VOCs.  $TiO_2$  and its derivatives can be excited by UV and visible light.  $TiO_2$  NPs doped with Ni and N ions. In recent years, doping metals and non-metals in the structure of the Titania have been the subject of much research to reduce the bandgap and use Titania under visible light to remove organic matter. This increases the surface area, absorbs contaminants on the photocatalyst surface, and carries the anatase phase of the Titania into the visible light region. Each doped material in the lattice structure creates new conditions in the photocatalyst activity. For pure Titania, absorption occurs in the ultraviolet region by electron excitation from the O2p orbital to the 3d titanium orbital. The displacement of the red line in doping causes new occurrences in the energy layer and the Such an energy bandgap. layer causes displacement in the bandgap and the red line in the electron transfer from the capacitance band to the conduction band in the TiO<sub>2</sub> structure. The

displacement of the main peak to the left or right indicates the presence of doping material in the photocatalytic lattice structure. In the present study, the photocatalyst was prepared using the sol-gel method. For a better study, the molecular ratio of silica-based titanium dioxide was changed to  $(Ti/Si=\frac{36}{64},\frac{27}{73},\frac{45}{55})$ . The resulting nanostructure was calcined at 1200 °C, and SEM, XRD, FTIR, and TGA techniques were used to analyze the nanostructure. The results show the thermal stability of the nanostructure up to 1200 °C. Also, the decomposition of MB as an organic pollutant was tested by the catalyst. The results show that 44% percent of the pollution has been removed. According to the study's main objective, i.e., investigation of the thermal stability of titanium dioxide using nanophotocatalytic doping materials at high temperatures, the results show that these materials maintain their stability up to 1200 °C. Therefore, the catalyst obtained can be used in the tile industry as a coating. The stability of titanium dioxide and the structural nondegradability are essential in the tile production process, performed at high baking temperatures. In addition, in some industrial applications, such as preserving self-cleaning properties surface, it is necessary to avoid using chemical detergents to protect the environment.

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## **Disclosure statement**

The authors declare that they have no conflict of interest

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