

IN SITU SYNTHESIS OF THE NOVEL PANI/TiO₂ PHOTOCATALYSTS FOR AZO DYE DEGRADATION IN WASTEWATER

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ABSTRACT

Titanium dioxide (TiO₂; Aeroxide® P25) is one of the most famous commercial photocatalyst. TiO₂ is non-toxic, environment friendly but with relatively high band gap of 3.2 eV that restricts its photocatalytic activity under the visible light. There were several attempts to increase the TiO₂ activity under the visible light (> 400 nm) by doping and by controlling the surface/particle size. However, the above attempts require the novel TiO₂ preparation. The most promising solution is to prepare P25-composites by using conductive (π -conjugated) polymers such as polyaniline (PANI), since it is non-toxic, thermally stable and they have a high absorption coefficient in the visible light region. When the PANI/TiO₂ composite is irradiated by visible light, the PANI excited-state electrons are formed which are easily injected into the TiO₂ conduction band (CB). Consequently, the injected electrons produce the superoxide radicals that oxidize the organic (dye) pollutant. The above mechanism, which enables the TiO₂ photoactivity under the visible light, is one part of the synergic PANI/TiO₂ effect. PANI/TiO₂ composites can be prepared by chemical in situ oxidation of aniline (An) in the presence of TiO₂ by using ammonium persulfate (APS). However, the PANI conductivity is governed by the experimental conditions that should be carefully chosen: concentration of An and APS, m(An):m(TiO₂), n(An):n(APS), type of acid, pH, etc. Obtained photocatalytic results (Fig.1) show achieved synergic PANI/TiO₂ effect as the dye removal is higher for 10% PANI/TiO₂ than for the pure TiO₂.

Keywords: titanium dioxide, polyaniline, composite, photocatalyst, azo dye

1. INTRODUCTION

Nowadays, organic synthetic (e.g. azo) dyes present one of the major environment pollution problems that originate from textile and dye industries. To dismiss the possibility of pollution, the organic dyes should be removed from waste waters by both decolorization and complete mineralization. One of the most efficient approach to perform the organic dye degradation is to use Advanced oxidation processes (AOPs) with intention of converting dyes to non-toxic and non-hazardous components.

Titanium dioxide (TiO₂; Aeroxide® P25) is one of the most famous commercial photocatalyst, which is non-toxic, environment friendly and very cheap to produce. However, its relatively high band gap (3.2 eV [1]) restricts its photocatalytic activity under the visible light. The TiO₂ activity under the visible light (>400nm) can be increased by doping and by controlling the surface/particle size, which requires the novel TiO₂ preparation. P25 was already proven as one of the most efficient photocatalysts, thus it should be modified with intention to increase its photocatalytic activity under the visible light. The most promising solution is to prepare P25-composites by using π -conjugated polymers such as polyaniline (PANI [2]), since it is non-toxic, thermally stable and it has a high absorption coefficient in the visible light region.

The TiO₂ photocatalytic performances can be drastically decreased due to recombination of UV excited electrons (e⁻) and holes (h⁺) [1]. The recombination process in TiO₂ can be hindered when using the PANI/TiO₂ composites, since PANI has ability to accept h⁺ from the TiO₂ valence band (VB) [3]. Furthermore, under the visible irradiation e⁻ from PANI LUMO are transferred to PANI HOMO [2, 3] and consequently injected into CB of the TiO₂, which forms the excess of e⁻. Therefore, the synergic PANI-TiO₂ effect (under the UV and visible irradiation) contributes to the excess of e⁻ in CB of the TiO₂.

The PANI/TiO₂ composites can be prepared by chemical in-situ oxidation [3] of aniline (An) in the presence of TiO₂, by using ammonium persulfate (APS). In order to obtain the synergic PANI-TiO₂ effect, PANI should be in its conductive and a most stable state. However, the PANI properties (e.g. conductivity) are

governed by the synthesis conditions [4] that should be carefully chosen: concentration of An and APS, $m(\text{An}):m(\text{TiO}_2)$, $n(\text{An}):n(\text{APS})$, type of acid, pH, etc. The objective of this work is to prepare PANI/TiO₂ composite photocatalysts, to investigate the photocatalytic activities and to confirm that the synergic PANI-TiO₂ effect was obtained.

2. EXPERIMENTAL

2.1. PANI/TiO₂ photocatalysts nanocomposites synthesis

Starting materials to prepare nanocomposites were: aniline (An), ammonium-persulfate (APS), commercial TiO₂ (P25) and sulfuric acid (H₂SO₄). The PANI/TiO₂ composites were prepared by in-situ chemical polymerization of PANI by using ammonium-persulfate (APS) as oxidant in the presence of the TiO₂ particles. The mole ratio of An:APS was constantly 1:1.25 and its influence on the synthesis can be seen here [4]. The PANI/TiO₂ samples were prepared by using the predetermined weight ratio of $m(\text{An})/m(\text{TiO}_2)$ (1, 5 and 10 %) and the obtained samples were designated as 1, 5 and 10PANI/TiO₂. The arbitrary chosen TiO₂ mass was 4 g. The 1PANI/TiO₂ was prepared by using the following solutions: aqueous solution A (50 ml) was prepared by using 4 g TiO₂ and 0.055 ml H₂SO₄ which was sonicated for 15 min to obtain stable suspension; aqueous solution B (50 ml) was prepared by using 0.039 ml An and 0.055 ml H₂SO₄ and aqueous solution C (50 ml) was prepared by using 0.123 g APS and 0.055 ml H₂SO₄. The solutions A and B were added into the reactor (200 ml) and obtained suspension was stirred (500 rpm) for 15 min to stabilize An and TiO₂. The in-situ polymerization was initiated by adding solution C into the reactor and filling with H₂O to reach the total reaction volume of 200 ml. The polymerization solution was stirred for 24 h at the room temperature and the obtained green product was washed using centrifuge. The obtained precipitate was dried for 24 h at 60 °C. The procedure to prepare samples 5 and 10 % PANI/TiO₂ was identical to former one, however one has to pay attention when adding An and APS to solutions B and C (Table 1). The pure PANI was prepared analogously as 10PANI/TiO₂ without the TiO₂ addition.

Table 1. The components used to prepare solutions A-C for the PANI/TiO₂ photocatalysts synthesis.

Sample	1PANI/TiO ₂	5PANI/TiO ₂	10PANI/TiO ₂	Pure PANI
$m(\text{An})/m(\text{TiO}_2) / \%$	1	5	10	-
$m(\text{TiO}_2)/ \text{g}$	4	4	4	0
$V(\text{An})/ \text{ml}$	0.039	0.196	0.392	0.392
$m(\text{APS})/ \text{g}$	0.123	0.613	1.225	1.225
$V(\text{H}_2\text{SO}_4)/\text{ml}$	0.055	0.055	0.055	0.055

2.2. Characterization

Samples were recorded by using Perkin-Elmer Spectrum One FT-IR spectrometer with the range of 4000–650 cm⁻¹. UV-Vis spectra were made over the range 200 to 800 nm at a spectral resolution of ~0.3 – 10 nm using UV/Vis spectrometer Ocean Optics USB 2000+. SEM images were obtained by thermal field emission scanning microscope (FE-SEM, model JSM-7000F). TEM images were obtained by transmission electron microscope (FEI Tecnai FEG20). Conductivity of PANI/TiO₂ composites was measured by a four-point probe method (Keysight 34461 61/2 Digit Multimeter). Thermogravimetric analyses (TGA) of samples were performed by using a TA Instruments Q500 analyzer. The results were obtained in temperature range from 25 to 800 °C at heat rate of 10 °C/min under nitrogen.

2.3. Photocatalytic activity test

The PANI/TiO₂ synergy effect was investigated by using the waste water solution containing 30 mg/L of azo dye (Reactive Red 45) and 1g/L of photocatalyst. The solution(s) was added into the glass water-jacketed batch reactor equipped with the Pen-Ray UVP lamp emitting irradiation in UVA region (315 to 400 nm), which was located in the middle of the reactor. The total volume of stirred (250 rpm) solution during experiments was 75 ml. Decolorization and degradation of RR45 in solution was monitored by a Perkin Elmer Lambda EZ 201 UV/VIS spectrophotometer where the absorption was measured at a wavelength of 542 nm for RR45. Total organic carbon (TOC) was determined after the photocatalysis by Total Organic Analyzer: Shimadzu TOC-VCPN.

3. RESULTS AND DISCUSSION

The synergic PANI-TiO₂ effect and improved photocatalysts performances can be obtained only if PANI in composites is conductive. Therefore, samples were first characterized by FT-IR. The pure doped PANI spectrum is presented in Fig. 1. The N-H stretching mode is located at 3257 cm⁻¹. The bands positioned at 1583 cm⁻¹ and 1494 cm⁻¹ represent C=N and C=N stretching modes for the quinoid (Q) and benzoid (B) units. C-N stretching modes at 1298 cm⁻¹ and 1236 cm⁻¹ are attributed to C-N stretching modes of the B units while bands at 1143 cm⁻¹ and 816 cm⁻¹ represent C-H vibration out the B ring. Overall, the intensity ratio of bands typical for Q and B indicates that the pure PANI is in the conductive form.

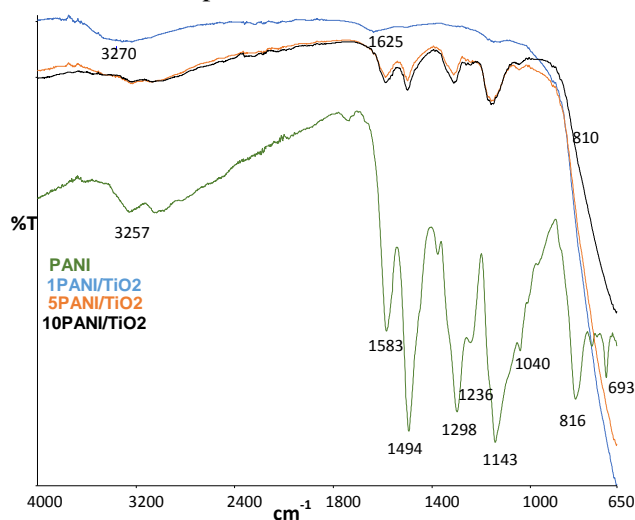


Figure 1. FT-IR spectra of the pure PANI and 1, 5 and 15PANI/TiO₂ composites.

1PANI/TiO₂ spectrum shows typical bands at 3270 and 1625 cm⁻¹ that are attributed to stretching and bending vibrations of the OH groups on TiO₂. Decrease in transmission at numbers lower than 900 cm⁻¹ is expected due to presence of TiO₂. The 1-10PANI/TiO₂ spectra present increase in intensity of bands around 1583 cm⁻¹ and 1494 cm⁻¹ which is expected due to the higher PANI content. The higher amount of PANI also increases the conductivity of composites which is presented in Table 2.

Table 2. PANI/TiO₂ composites conductivity.

Sample	1PANI/TiO ₂	5PANI/TiO ₂	10PANI/TiO ₂
Conductivity / S cm ⁻¹	1.21 10 ⁻⁶	2.74 10 ⁻⁵	2.76 10 ⁻⁵

It should be noted that the most prominent shift in the bands intensities and samples conductivity is observed when comparing 1 and 5PANI/TiO₂ composites, which indicates that strong PANI-TiO₂ interaction occurs at the higher PANI adding. The low 1PANI/TiO₂ conductivity ($\approx 10^{-6}$ S cm⁻¹) indicates the possibility that parts of the PANI layer have characteristic ($\approx 10^{-8}$ S cm⁻¹) of reduced and non-protonated PANI [4]. To summarize, the FT-IR and conductivity values indicate i) the strong PANI-TiO₂ interaction and ii) that PANI is in the conductive form, both of which are essential for the synergic PANI/TiO₂ effect.

The UV-Vis reflectance spectra of TiO₂, PANI and PANI/TiO₂ composites are presented in (Fig. 2). The pure TiO₂ reflected > 80 % of irradiation, whereas the pure PANI reflected only < 10 %. The UV-Vis spectra indicate significant difference in the composites reflectance intensity, which is decreased due to the higher amount of PANI in composites.

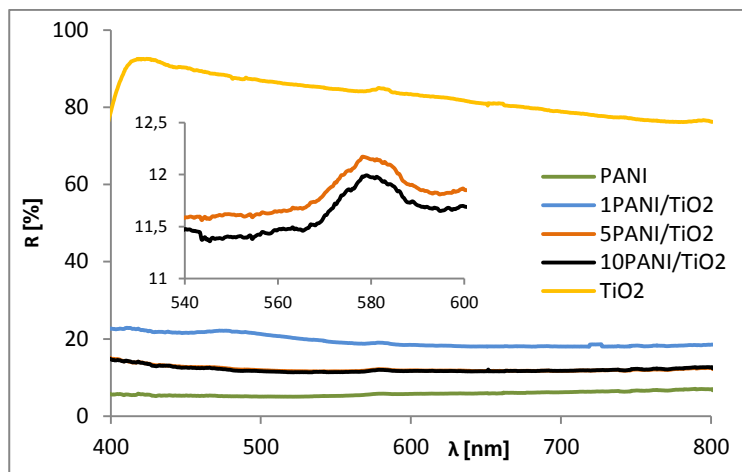


Figure 2. UV-Vis reflectance spectra of TiO_2 , pure PANI and PANI/ TiO_2 composites

The most drastic variation in reflection values is observed for 1 and 5PANI/ TiO_2 composites which is in agreement to both FT-IR spectra and conductivities values. The lowest reflectance is obtained for 10PANI/ TiO_2 sample which indicates that the TiO_2 particles are covered/coated by a uniform PANI layer. The above statement is confirmed by the FE-SEM images of pure TiO_2 and 10PANI/ TiO_2 which indicates that size of the TiO_2 particles in the composite (Fig. 3b) is rather similar to size of the pure TiO_2 (Fig. 3a).

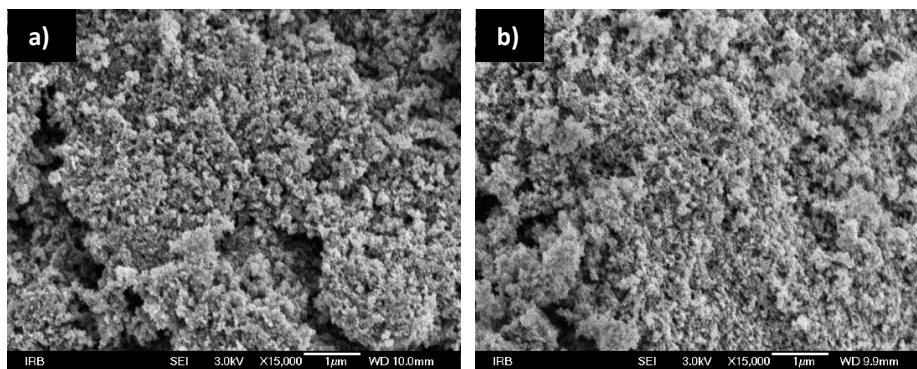


Figure 3. FE-SEM micrographs of a) TiO_2 and b) 10PANI/ TiO_2 nanocomposites.

Thus, the experimental conditions for in-situ PANI synthesis used in this work enabled formation of the thin and uniform PANI layer on TiO_2 particles. The presence of the larger aggregates (Fig. 3b) indicates a possibility that smaller amount of TiO_2 was captured in a PANI matrix during the in-situ synthesis.

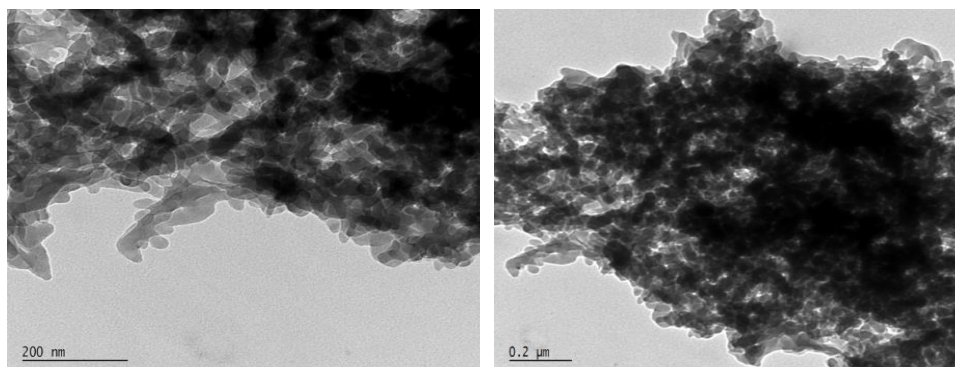


Figure 4. TEM images of 10 PANI/ TiO_2 sample.

Additionally, the uniform appearance and compact morphology of the layer suggest that the PANI layer is consisted of a long and relatively unbranched PANI chains. The compact layer indicates that the in-situ

PANI polymerization mainly took place at the TiO_2 surface which reduced the formation of aggregates, i.e. only a small amount of TiO_2 particles were captured in the PANI matrix.

In order to investigate the effect of the immobilized PANI onto TiO_2 , PANI/ TiO_2 composites were used in photodegradation processes of the RR45 waste water (Fig. 5). Prior to photodegradation and decolorization processes, solutions were stirred for 60 min in the dark to obtain the adsorption/desorption equilibrium between photocatalysts and RR45 dye.

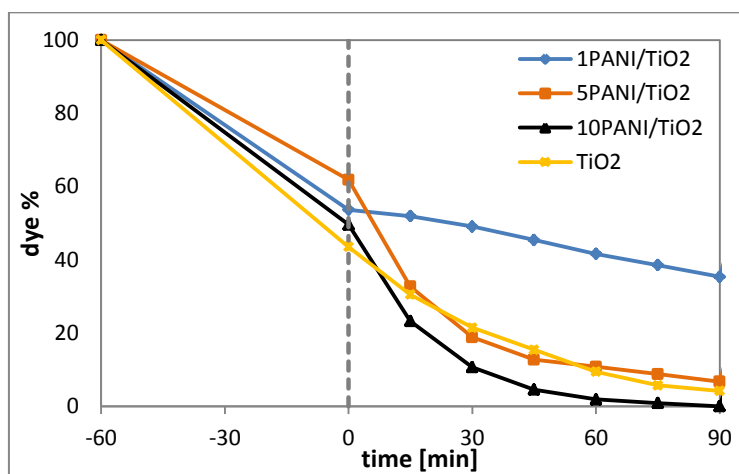


Figure 5. Decolorization rate of Reactive Red 45 during adsorption and photocatalysis using TiO_2 and synthesized PANI/ TiO_2 composites ($\gamma_{\text{RR45}}=30 \text{ mg/L}$, $\gamma_{\text{PANI/TiO}_2}=1 \text{ g/L}$, $\text{pH}=4$)

It can be seen that after 60 min, the TiO_2 particles presented the highest ability to adsorb the RR45 dye. However, the high TiO_2 ability to adsorb dye (or dye intermediate) can decrease the bare TiO_2 activity in the repeated cycles [3]. On the other hand, the sample with the highest amount of PANI (10PANI/ TiO_2) removed the highest quantity of dye in comparison to other composites. The lower adsorption ability of 10PANI/ TiO_2 vs. TiO_2 can be explained by the fact that a small amount of the TiO_2 particles is captured within the PANI matrix (Fig. 3b). After the adsorption/desorption period (Fig. 5), the degradation of RR45 has started (0 to 90 min). During the UV-Vis treatment, 10PANI/ TiO_2 removed the highest amount of the RR45 dye which is improved performance when compared to the pure TiO_2 . It should be noted, that the presence of PANI in composites additionally stabilized the photocatalytic activity during the repeated experiments [3], which indicates that PANI does not degenerate during the experiments. Unlike the 10PANI/ TiO_2 sample, 1PANI/ TiO_2 removed less dye in comparison to the pure TiO_2 . It follows that 1PANI/ TiO_2 is covered by the PANI layer that is to a small degree consisted of the nonconductive polymer (i.e. oligomers). The low An concentration could promote the formation of the small nonconductive oligomers [4], which do not form a chemical interaction with a $-\text{SO}_3^-$ group of the dye [5]. Thus, the dye adsorption in the case of 1PANI/ TiO_2 is additionally hindered if the nonconductive oligomers covers TiO_2 surface (Fig. 5).

The RR45 dye from waste water can be removed in two ways by process of dye adsorption onto the photocatalyst or by photocatalytic degradation of dyes. Thus, during the photocatalytic degradation of dyes the degradation process can be partial, e.g. the degradation of chromophore group, which is followed as discoloration presented in Fig.5. In order to monitor the complete process of RR45 degradation it was necessary to determine the total organic carbon (TOC) in waste water after photocatalysis. Fig. 6 present TOC values (%) that were removed from the starting RR45 waste water.

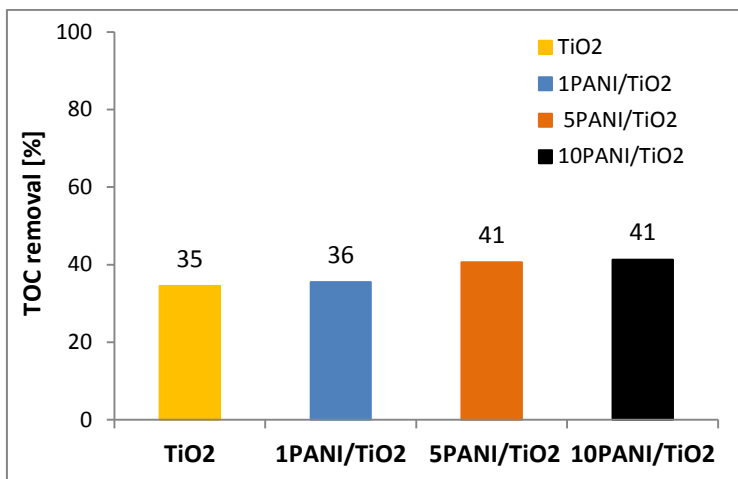


Figure 6. Variation in TOC removal (%) for investigated photocatalyst samples.

The best TOC removal performance was obtained by 5 and 10PANI/TiO₂ samples (41 %), whereas the poorest one was offered by TiO₂ (35 %). TOC values for the studied photocatalysts are in agreement to the decolorization rate (Fig. 5). However, 1PANI/TiO₂ removed 36 % TOC which is slightly unexpected due to the lowest decolorization rate. The above fact indicates that the nonconductive oligomers in the 1PANI/TiO₂ layer blocked the dyes adsorption on the composite which resulted with the poorest decolorization process (Fig. 5). On the other hand, the conductive PANI part of the layer enabled the synergic PANI-TiO₂ effect which in turn yielded the similar TOC removal performances as the pure TiO₂.

The presence of the immobilized PANI layer in 10PANI/TiO₂ resulted in improved photocatalytic performances when compared to the pure TiO₂. Therefore, to determine the stability of PANI layer 10PANI/TiO₂ samples were characterized by TGA before and after photocatalysis (Table 3 and Fig. 7.)

Table 3. TGA results of 10PANI/TiO₂ sample characterized before and after photocatalysis: temperature at maximum degradation rate (T_{max}), carbon residue and rate of thermal degradation (r).

Samples	T_{max}	residue / %	r (%/min)
10PANI/TiO ₂	501.25	86.38	0.6524
10PANI/TiO ₂ after 90 min of photocatalysis	514.21	85.65	0.8779

Fig. 7 indicates that after 90 minutes of photocatalysis, the temperature at maximum degradation (T_{max}) of PANI rate was slightly increased which can be explained by strong dye (or dye intermediate) PANI interaction [5] and residue of RR45 on the catalyst. The fact that residue value was not significantly decreased after 1 photocatalytic cycle indicates that PANI is stable in the 10PANI/TiO₂ composite. It is assumed that reduction of residue represent degradation of PANI oligomer as indicated in Fig. 7 a) by T_{max} at 407 °C.

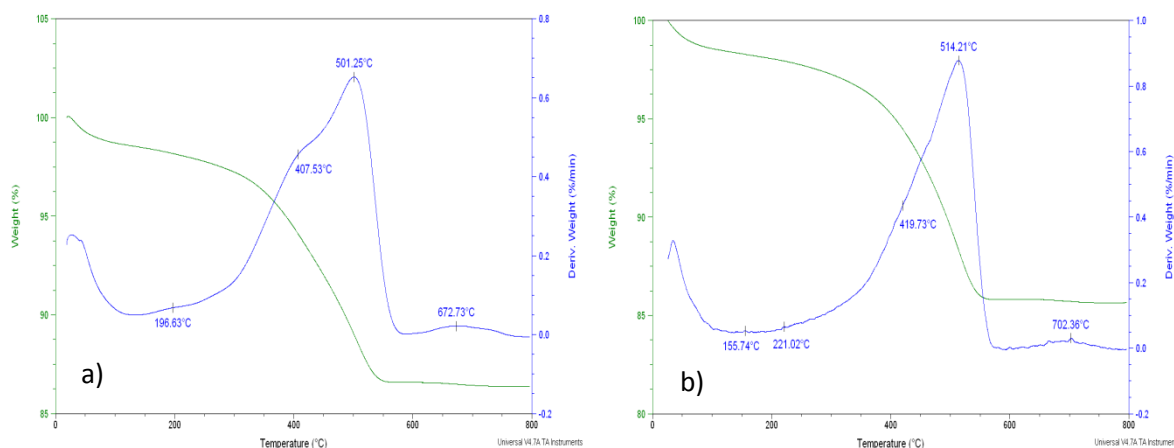


Figure 7. TG and dTG curves of 10PANI/TiO₂ sample characterized a) before and b) after photocatalysis.

4. CONCLUSION

PANI/TiO₂ nanocomposites photocatalysts were successfully prepared by the in-situ oxidative polymerization of aniline. It was presented that the conductive PANI layer on TiO₂ can be immobilized in a weak acidic media. PANI in nanocomposites was in the conductive state which was confirmed by FT-IR and conductivity measurements. In the case of the 10PANI/TiO₂, FE-SEM and TEM images showed that the PANI layer was uniformly formed at the TiO₂ surface which enabled the synergic PANI-TiO₂ effect that yielded the best composite photocatalytic performance. The stability of the PANI layer in 10PANI/TiO₂ was confirmed by TGA, i.e. the PANI mass loss was not detected after the photocatalytic degradation. On the other hand, the existence of the nonconductive oligomers in the 1PANI/TiO₂ sample partially blocked the dye adsorption which yielded the lowest decolorization rate. However, the presence of the conductive PANI in layer enabled the synergic effect and consequently the similar TOC removal was obtained by 1PANI/TiO₂ and TiO₂ samples.

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