

SYNTHESIS AND CHARACTERIZATION OF TITANIA NANOTUBE-CARBON NANOTUBE COMPOSITE FOR DEGRADATION OF PHENOL

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ABSTRACT

Titania nanotube (TNT)-carbon nanotube (CNT) composite had been successfully synthesized using simple mixing under acidic conditions and ultrasonic treatment. The samples were further characterized via field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), diffuse reflectance UV-vis spectroscopy, and Brunauer-Emmett-Teller (BET) analysis. The TNT-CNT composite's ability to degrade phenol, a model of industrial waste, was tested. The effects of CNT composition and calcination temperature on the phenol degradation performance of TNT-CNT composite were investigated. The results show that the TNT-CNT composite exhibits higher photocatalytic activity than TNT or CNT alone. The crystallinity of the catalyst is not the only parameter affecting the photocatalytic activity. Rather, the specific surface area, bandgap, and morphology of the catalyst must also be considered.

Keywords: Degradation; Phenol; Photocatalysis; Titania nanotube - Carbon nanotube composite

1. INTRODUCTION

Currently, photocatalytic technology has attracted much attention from scientists around the world due to its wide range of potential applications, especially in waste water treatment. A photocatalytic chemical reaction is a process that is aided by the presence of light and semiconductor photocatalyst materials (Serpone, 2002). When exposed to the light (of a certain wavelength), photocatalyst material will generate electrons and hole pairs (e^-/h^+), which can be used in simultaneous reduction/oxidation reactions to degrade pollutants (heavy metals ion, inorganic, or organic compounds).

One type of semiconductor photocatalyst that is often used is titanium dioxide (TiO_2) or titania in the form of nanoparticles due to its relatively high photocatalytic activity, biological and chemical stability, low cost (its source of energy is the photons of light, which could be generated from the sun), non-poisonous, and long lifespan (Shifu & Gengyu, 2005; Luo et al., 2009; Rao et al., 2003). It has been proven that photocatalysts such as TiO_2 can degrade pollutants effectively, producing only harmless compounds such as H_2O and CO_2 (Dumitriu, 2000). In further research, titania nanoparticles' form (or morphology) has been successfully modified into a nanotube form (Kasuga et al., 1999). Titania *nanotubes* have been widely developed because of their good electronic and mechanic characteristics, high photocatalytic

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activity, large surface area and pore volume (Wong et al., 2011). Titania with a nanotube morphology may be able to interact relatively more easily with other materials as compared to titania nanoparticles.

However, especially for waste water treatment, photocatalytic technology itself still has several weaknesses that limit its use: low adsorption ability and a high rate of electron-hole recombination, which lower its efficiency. Regarding this issue, it is important to combine semiconductor photocatalysts with other materials to enhance their performance. Adding a co-adsorbent, such as carbon nanotubes (CNT) is a good strategy to enhance the photocatalytic efficiency of titania nanotubes. It has been reported that CNT has many special characteristics, such as unique electrical properties, high chemical stability, and high adsorption ability (Jiang et al., 2013). Other studies also show that the adsorption ability of CNT may increase the photodegradation activity of TiO₂ (P25) (Yu et al., 2005).

During the recombination process, the presence of CNT on the surface of the photocatalyst may bind electrons released by titania, acting as an electron trapper, which would prevent the occurrence of the electron-hole recombination process. Eder and Windle (2008) showed that the interaction between TiO₂ nanoparticles and CNT improves photocatalytic properties in three ways: storing or trapping electrons, creating band gap energy, and allowing visible light absorption. Though the combination of CNT and TiO₂ nanoparticles has been widely inspected and developed, studies to investigate the effect of CNT's presence in/on TNT in terms of photocatalyst characteristics and photodegradation performance remain infrequent.

The development of photocatalysis technology is very related to many problems that humans must face, such as waste treatment problems. One of the waste component that is usually found and is very difficult to be treated is phenol. Phenol is often released into the environment without further treatment (Wong et al., 2011), though phenol itself is included among the toxic and carcinogenic compounds, which are hazardous to humans (Wong et al., 2011). Various methods to remove and degrade phenol components in waste have been widely developed, including adsorption, biodegradation, extraction using liquid membranes, and oxidation, as in ozonation and photocatalysis (Gondal & Seddigi, 2006). It has been proven that the usage of photocatalysis technology can degrade phenol effectively (Wong et al., 2011; Slamet et al., 2010).

Based on this, a study to produce a modified photocatalyst, a TNT-CNT composite, with good performance in the degradation of phenol pollutants becomes an interesting and strategic topic. In this study, TNT-CNT composite was synthesized by combining TNT and varied amounts of CNT catalyst using simple mixing and ultrasonic treatment. The prepared composite was tested for its ability to photodegrade phenol. This study aims to investigate the effect of CNT composition (w/w %) and calcination temperature on the phenol degradation performance of TNT-CNT composite.

2. METHODOLOGY

2.1. Material

CNT (multi-walled CNT) was purchased from Dong Yang (HK) Intl Group Limited Hongwu Nanometer. Its specifications are as follows: purity, 99%; size diameter, 10-30 nm; length, 5-15 μ m, and it had been pre-treated using acid (HNO₃ 65%). Phenol powder, TiO₂ P25 with a crystallographic mode of 79% anatase and 21% rutile, a surface area of 53.6 m²g⁻¹ BET (Slamet et al., 2005), and an average particle size of 21 nm was purchased from Evonic Industries. Sodium hydroxide pellets and fuming hydrochloric acid for the preparation of titania nanotubes (TNT) were purchased from Merck and Mallinckrodt, respectively.

2.2. Synthesis of TNT-CNT Composites

TNT is synthesized using a hydrothermal process. TNT was prepared by dissolving 6 gram of TiO_2 P25 powder into 300 mL of 10 M NaOH solution, followed by ultrasonication for 30 min. The mixture was transferred into a Teflon-lined stainless steel autoclave and crystallized at 130°C for 6 h under continuous stirring at 600 rpm (Slamet et al., 2012). Then, the autoclave was cooled to room temperature, and the precipitate was filtered and washed with hydrochloric acid and deionized water until a neutral precipitate was obtained. The product was further dried. CNT was first acid treated (using HNO_3 65%) and then washed with distilled water until a pH of 3 was achieved (Zhang et al., 2006). Then, sol of photocatalyst TNT (mixture of TNT and certain amount of water) was made on the pH of 3. Each of the mixtures was further ultrasonicated for 1 hour. Both liquids were mixed and ultrasonicated again for 1 hour (Vijayan et al., 2012). TNT-CNT composite powder was then obtained after drying at 80°C for several hours and calcined at a high temperature for 2 hours in a nitrogen atmosphere (Ouyong et al., 2013). The amount of CNT in the composite was varied: 3 wt.% , 5 wt.% , and 10 wt.%. The calcination temperature was also varied: 400°C and 500°C .

2.3. Performance Test of Photocatalyst

A performance test of the photocatalyst was performed by measuring the phenol photodegradation efficiency of TNT-CNT composites. Phenol synthetic wastewater (10 mg/L) was prepared by dissolving powdered phenol in 300 mL of water. The test was performed in an open reactor placed in a closed test box, which is lined with aluminum foil. In the box, there was a PHILIPS HPL-N mercury lamp with 250 W power and $165 \mu\text{m}/\text{cm}^2$. The reactor was equipped with a magnetic stirrer, which was turned on during the performance test to ensure the reaction took place homogeneously. The test box is also equipped with a blower to control the temperature within the test box. Then, the liquid samples were drawn from the reactor, starting at 30, 20, and 10 minutes before the lamp was switched on and continuing frequently (every 30 minutes) thereafter during the 240 minutes of the performance test. The samples were analyzed using a UV/Vis spectrophotometer using Spectroquant Pharo 300, with the measured parameter being phenol concentration.

3. RESULTS AND DISCUSSION

Figure 1 presents the FE-SEM image of TNT (Figure 1a) and CNT (Figure 1b). Figure 2 shows the FE-SEM image of TNT-CNT composite with different CNT weight ratios.

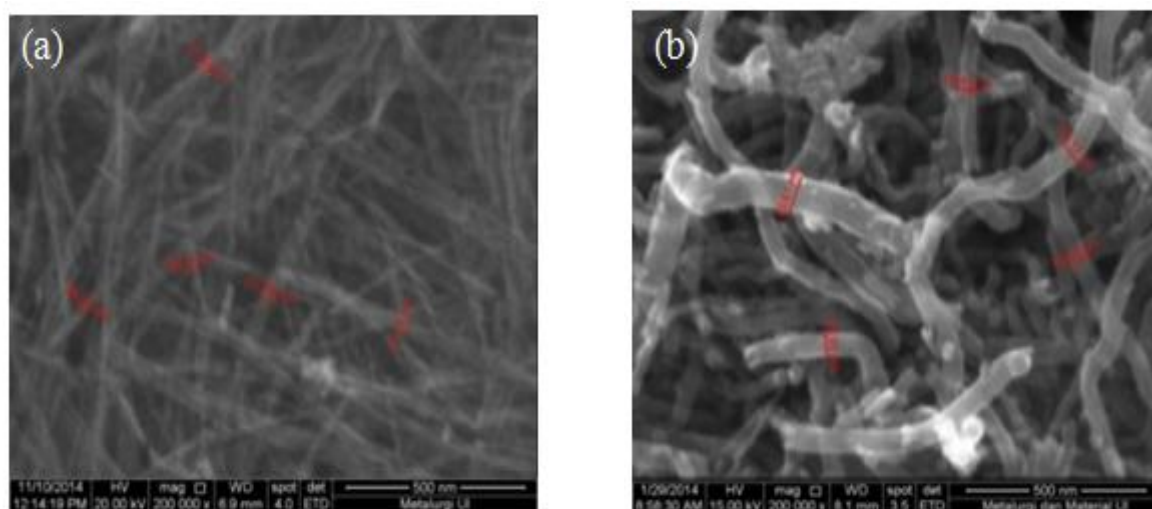


Figure 1 FE-SEM image of: (a) TNT ; (b) CNT

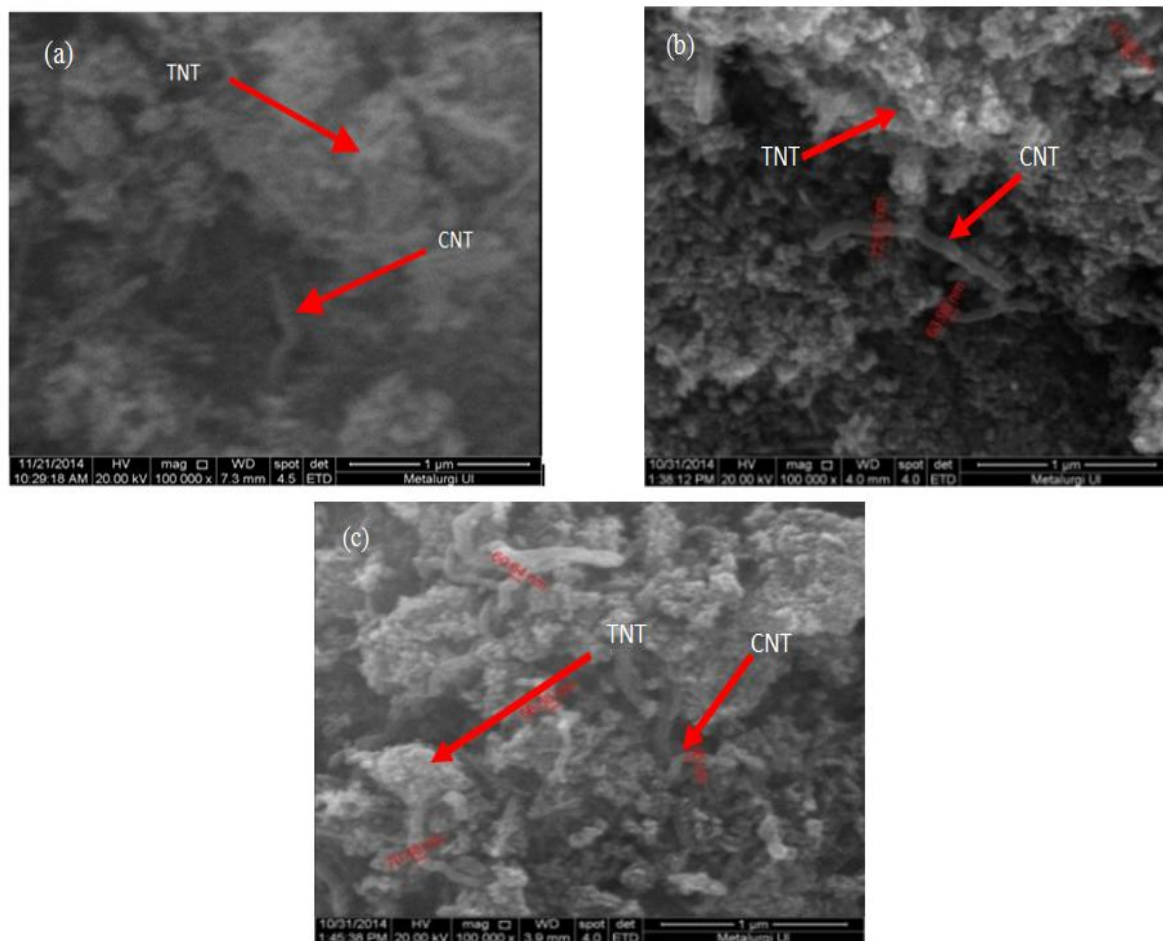


Figure 2 FE-SEM image of TNT-CNT composite, CNT of : a) 3 wt.%; b) 5 wt.%, and; c) 10 wt.%.

From Figures 1a and 1b, it can be seen that the morphology of TNT and CNT was supposed to resemble a tube. However, Figure 2 shows that the morphology of the TNT in the TNT-CNT composite changed its shape into something like a sphere, while the morphology of the CNT was maintained. The change in TNT morphology after the TNT-CNT composite synthesis process was probably caused by the sonication treatment, which may have affected the structure of the TNT due to the great strength of the sonication wave. The ultrasonic treatment was first used for the purpose of decreasing the size of the particles and dispersing the particles homogeneously. However, in this study, it may not affect only the macrostructure of catalyst but also the nanostructure. It is important to know that before the calcination process, the TNT catalyst was very fragile because of the presence of nanopores in the wall of TNT. This explains why the ultrasonic treatment may have changed the shape of the TNT.

The second potential reason for this phenomenon is related to the calcination process used for the composite, which was performed in a nitrogen atmosphere (N_2). The presence of N_2 would lead to the loss of oxygen atoms, forming oxygen vacancies, which may have attracted N atoms, forming O-Ti-N bonds. In an O-Ti-N bond, the electrons move from N to Ti, which causes electron density and makes the structure of TNT tend to be curly tubes (Liu et al., 2012).

Figure 2 also shows the direct interaction between TNT and CNT to form the composite. The TNT-CNT composite is interwoven because of the functional groups of the CNT wall ($-COOH$, $C=C$) as the result of the acid treatment, which would interact with TNT, containing hydroxyl-group-bonding Ti-O-Ti, to create Ti-O-C or Ti-C bonding (Vijayan et al., 2012). In addition, the TNT-CNT composite is interwoven due to electrostatic bonding, which may occur because

of the negative charge of CNT and the positive charge of TNT under acidic conditions (Vatanpour et al., 2012).

Figure 3 shows the XRD pattern of TNT and TNT-CNT composites that were calcined at 400°C and 500°C. Anatase crystallite size after calcination were calculated using the Scherre equation and can be seen on Table 1.

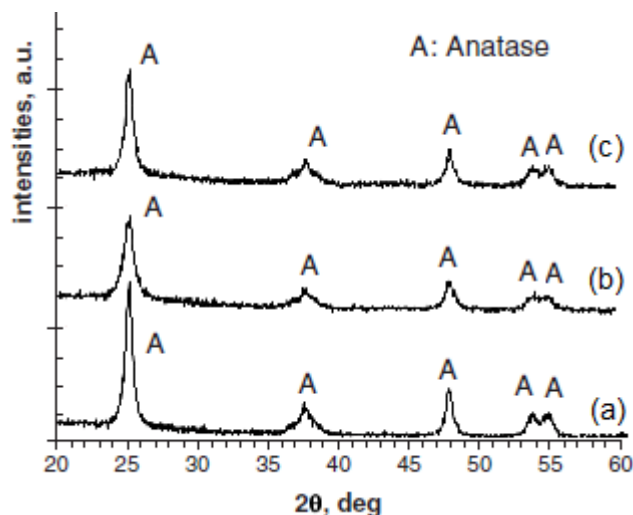


Figure 3 XRD patterns of : a) TNT; b) TNT-CNT composite ($T_{\text{calcination}}$: 400°C); and c) TNT-CNT composite ($T_{\text{calcination}}$: 500°C)

It can be seen in Figure 3 that both the TNT catalyst and TNT-CNT composite have peak intensities at 2θ : 25.28°, 37.87°, 48.10°, 54.04°, and 55.08°, which indicates the presence of an anatase crystalline phase (according to JCPDS no. 21-1272). The anatase peak of the TNT sample was found to be higher than that of the composite sample. This phenomenon may have occurred because in the case of the composite, the TNT was covered by CNT, obstructing the crystallization process of the TNT.

Table 1 The properties of the catalysts

Catalysts	Surface area (m ² /g)	Anatase Crystallite Size (nm)	Bandgap (eV)	Wavelength (nm)
CNT	200.0	–	–	–
TNT 500°C	116.4	10.9	3.20	388
TNT-CNT Composite 400°C	151.8	7.7	3.15	395
TNT-CNT Composite 500°C	70.2	9.9	3.10	401

The TNT-CNT composite calcined at 500°C was found to have a higher degree of crystallinity as compared to the composite calcined at 400°C. It can be concluded that a higher temperature of calcination accelerates the crystallization process of the photocatalyst. This also affects the size of the crystals. Table 1 showed that the crystal sizes of TNT at 500°C and TNT-CNT composite at 400°C and 500°C are 10.9, 7.7, and 9.9, respectively. A higher level of crystallinity will lead to greater photocatalytic activity.

Table 1 summarizes the BET surface area of various materials: 200 m²/g and 116.4 m²/g for CNT and TNT samples, respectively, showing that compared to TNT, CNT has significantly

increased surface area, probably due to the unique pore structure of CNT. TNT-CNT composites calcined at 400°C and 500°C had surface areas of 151.8 m²/g and 70.2 m²/g, respectively, which were lower than the surface area of CNT. This phenomenon probably occurred due to damage to the CNT structure caused by high temperatures (Jiang et al., 2013).

The obtained TNT-CNT composite was used in the phenol degradation performance test. Figure 4 shows the effect of CNT composition on the phenol degradation performance of TNT-CNT composites.

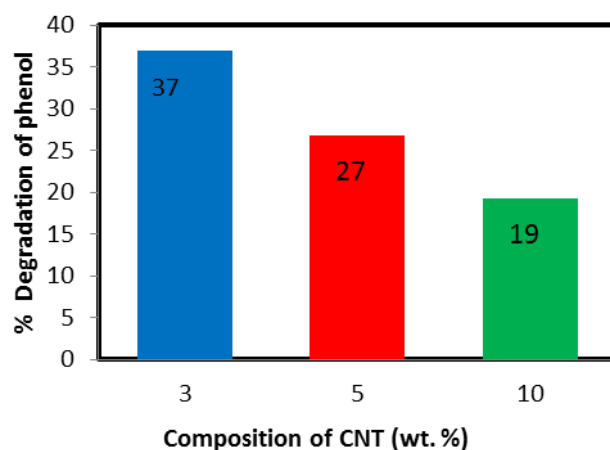


Figure 4 Effect of CNT composition on the phenol degradation performance of TNT-CNT composites

Figure 4 shows that the TNT-CNT composite with 3 wt.% of CNT had better phenol degradation performance (up to 37% of phenol degradation) than the other composites. A higher loading of CNT will decrease the photocatalytic activity of TNT because the CNT will cover the TNT, leaving it unable to receive photons and thus inactivated. Additional studies must investigate the effect of CNT loadings smaller than 3 wt.%, which may have better phenol degradation performance. The excessive dosages of catalyst could decreased yield of effective photon so that to lower photocatalytic activity (Jiang et al., 2013). A larger amount of CNT loading into the TNT-CNT composite causes stronger background absorption (Tang et al., 2011).

Figure 5 shows the effect of calcination temperature on phenol the degradation performance of the TNT-CNT composite.

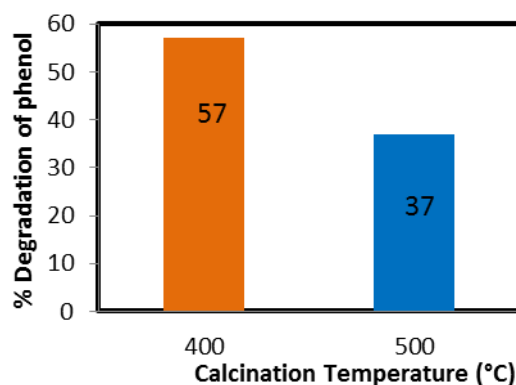


Figure 5 Effect of calcination temperature on the phenol degradation performance of TNT-CNT composite

Figure 5 shows that the TNT-CNT composite calcined at 500°C had better phenol degradation performance (up to 57 % phenol degradation). This could be explained by the fact that a higher temperature of calcination reduces the surface area of TNT significantly (Qamar et al., 2008). As seen in the BET results (Table 1), TNT-CNT composites calcined at 500°C and 400°C have surface areas of 70.18 and 151.8 m²/g, respectively. This may happen because the structure of the TNT-CNT composite is damaged by the high temperature of calcination (Jiang et al., 2013).

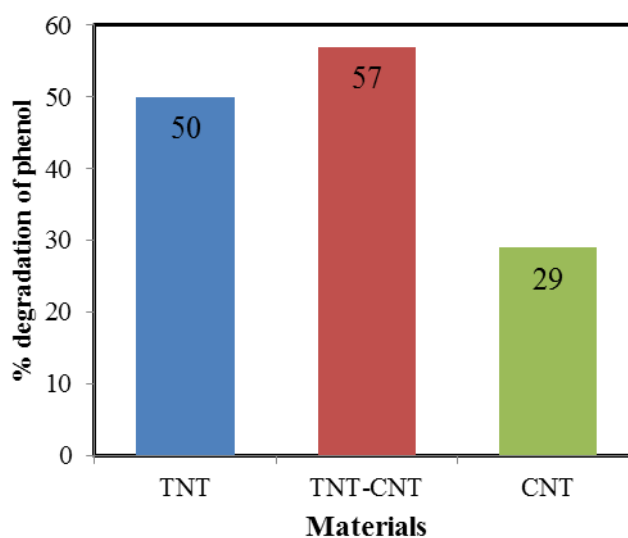


Figure 6 Phenol degradation of TNT, TNT-CNT, and CNT

Figure 6 shows the phenol degradation performances of TNT, TNT-CNT (with CNT composition of 3 wt.% and calcined using N₂ at 400°C), and CNT samples, which are 50%, 57%, and 29 %, respectively. This results indicate the improvement of the photocatalytic activity of TNT by combining it with CNT. The synergetic effect of CNT on the activity of the composite catalysts may be ascribed to the special structure and performance of CNT. CNT acts as an electron trapper within the conduction band of TiO₂, so the recombination of electron/hole (e⁻/h⁺) pairs could be effectively decreased, and CNT has a large surface area and various aperture structure. Thus, CNTs can adsorb oxygen on their inside or outside surfaces (Wang et al., 2011), so CNT acts as an adsorbent, supporting the photocatalytic degradation of phenol.

The UV-vis diffuse reflectance spectra (DRS) patterns of all the samples are shown in Figure 7. The figure shows that the spectra of TNT 500°C, TNT-CNT composite 400°C, and TNT-CNT composite 500°C exhibit good light absorption capability in the UV region. The composites of TNT-CNT show much higher light absorption capability than the sample of pristine TNT. This is indicated by the greater wavelength upon the formation of TNT-CNT composites as compared with pristine TNT (Table 1).

The presence of CNT in TNT-CNT composites causes a continuous absorption band in the 400-800 nm range. The absorption spectra were obtained by analyzing the reflectance measurement via the Kubelka–Munk emission function (Owen, 1996). As shown in Table 1, the bandgap for TNT calcined at 500°C was approximately 3.2 eV, which corresponds to the absorption of the 388 nm wavelength, whereas the modified photocatalyst with CNT exhibited an increased wavelength. The TNT-CNT composite (calcination of 400°C and 500°C) produced wavelengths of 395 nm and 401 nm, respectively (Table 1). This indicates that the photocatalyst responds positively to UV light.

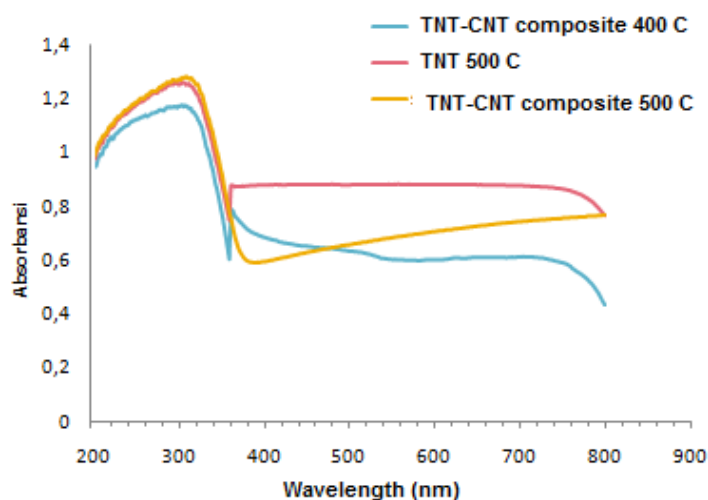


Figure 7 UV-vis DRS of samples of TNT and TNT-CNT composites

4. CONCLUSION

TNT-CNT composites were successfully obtained through simple mixing and ultrasonic treatment. The experimental results show that the TNT-CNT composite with 3 wt.% of CNT exhibits better phenol degradation performance (up to 37%) as compared to the other composites with various loadings of CNT, and TNT-CNT composite calcined at 400°C showed an even better phenol degradation performance (up to 57%). The crystallinity of the catalyst is not the only parameter that affects the photocatalytic activity. Rather, the specific surface area, bandgap, and morphology of the catalyst must also be considered.

5. ACKNOWLEDGEMENT

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