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SYNTHESIS OF CARBON NANOTUBE–TITANIA COMPOSITE FOR APPLICATION IN A SELF-CLEANING SELF-STERILIZING DIAPER

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ABSTRACT

A carbon nanotube–titania (CNT-TiO_2) composite that coats diapers has been synthesized and tested for the removal of ammonia (self-cleaning test) and *Candida albicans* fungi (self-sterilizing test), which cause unpleasant odors and candidiasis disease, respectively. The composite was characterized by FTIR, FESEM-EDX, XRD, and UV-Vis DRS. Results of XRD and UV-Vis DRS measurement showed that the CNT-TiO_2 composite has a high crystalline and low band gap. The results of the self-cleaning and self-sterilizing tests showed that the optimum composition of the composite was 1–3 wt% of CNT and 97–99 wt% of TiO_2. Acid treatment at pH 1 was accompanied by ultrasonic agitation in appropriate conditions for composite synthesis. Within 2 hours of testing, the modified diapers, at the optimum composite composition, can remove ammonia and *C. albicans* by 91% and 98%, respectively. The experimental results showed that ammonia and fungi on the modified diapers were removed up to the standard minimum values required to prevent odor and diaper rash.

Keywords: Ammonia; CNT; Candida albicans; Composite; TiO_2

1. INTRODUCTION

A diaper that has not been changed can cause an infant's skin to be irritated and infected by several types of bacteria and fungi. Approximately 50% of infants 3–12 months old will have irritated skin when using a diaper with improper care (Jaswin, 2013). This irritation is commonly called diaper rash. In addition to a yeast infection, an unchanged diaper will release an odor caused by ammonia. Ammonia in infant urine is at a low concentration of around 0.05%. However, even that level can have negative effects and is dangerous to our respiratory system. The minimum safe level of ammonia in solution is around 50 ppm (Minister of Environment No. 03/MENLH/1991). In addition to health problems, using diapers also causes environmental pollution problems because it is difficult to recycle or dissociate this diaper waste, which is in the form of fibers and plastics. Technology today has developed a modern diaper that is reusable. However, a reusable diaper cannot eliminate odors and diaper rash problems. In this research, we propose a concept of photocatalytic technology to eliminate ammonia and microbacteria in urine and deodorize the diaper.

The photocatalytic process is an advanced oxidation process with a high potential to degrade deodorized urine and dirt that has accumulated in the diaper. The basis of this method is the generation of reactive species, such as hydroxyl-free radicals, by using a catalyst that is activated by a photon from light at a specific wavelength.

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Titania (TiO_2) as a photocatalyst can potentially photodegrade the compounds of ammonia, converting them to a nitrogen–hydrogen compound that is less dangerous (Nemoto et al., 2007). In addition, a photocatalytic reaction has the potential to be used for safely disinfecting microorganisms in low concentrations (Kabir et al. 2003). The reaction can also disinfect microbacteria, such as bacteria and fungi, via an oxidation process into carbon dioxide and water, which is safer for the environment (Huang et al., 2000).

This study is focused on eliminating ammonia and disinfecting *Candida albicans* in diapers. A carbon nanotube–titania (CNT-TiO_2) composite is highly effective (Chong et al., 2010) in its absorption of ultraviolet (UV) light, so it can be used in place with less light. In this study, various composition of CNT-TiO_2 were tested to find the CNT-TiO_2 composites having optimal performance in removing ammonia and disinfecting fungus as well as being responsive to sunlight.

2. EXPERIMENT

2.1. Reagents and Materials

TiO_2 P25 was purchased from Evonik. Multi-walled carbon nanotubes, NH_4OH, HCl, HNO_3, H_2SO_4, and H_2O_2 were purchased from Merck. Reagent indofenol was based on SNI 19-7119.1-2005 (SNI, 2005). Pure culture of *C. albicans* was prepared with agar medium. Catalyst characterizations of the experiments were conducted with a Fourier transform infrared spectrophotometer FTIR (IR Prestige-21; Shimadzu), UV-Vis DRS (Spectrophotometer DRS-8000; Shimadzu), SEM/EDX (FE-SEM FEI INSPECT F50; Shimadzu), and an X-Ray diffractometer XRD (XD 610; Shimadzu).

2.2. Synthesis of CNT-TiO_2 Composite

Before being used, carbon nanotubes were calcined at 400°C for 15 minutes to ensure a crystallinity of carbon nanotubes. This was followed by reflux treatment in a 6 M HCl solution at a boiling temperature for 3 hours in order to remove metal catalyst particles. Following reflux, the black solution was centrifuged, leaving black sediment at the bottom and sides, and the sediment was dried. The clean and crystalline CNT was then functionalized by sonication for 30 minutes in a 1:1 (volume [v]:v) solution of 5 M HNO_3 and 30% H_2O_2 at 140°C for 24 hours. Following reflux treatment, the black solution was centrifuged again, leaving black sediment at the bottom and sides of the centrifuge tube. The sediment still contained substantial trapped acid, which was removed by repeatedly suspending the sediment in deionized water until a neutral pH was obtained. The resulting functionalized MWCNT was dried in a vacuum furnace at 110°C for 4 hours. We next created a TiO_2 solution with distilled water, which was stirred for a few minutes and then processed by sonication. After completion, the functionalized CNTs that were previously dissolved in water and the TiO_2 solution were mixed together with the sonication technique. The composite that formed was dried at a temperature of 80°C and was followed by calcination at 110°C for 4 hours.

To coat the composite on the diaper, CNT-TiO_2 powder was mixed with water and the pH of the mixture was adjusted. The composite and water mixture was stirred by the sonicator probe for 10 minutes. The composite was coated on the diaper by using a sonicator bath and was then dried several times. The process was repeated again until the superimposed composite of CNT-TiO_2 was exhausted. The diaper with the composite of CNT-TiO_2 was then dried at 110°C for 3 hours.

2.3. Ammonia Degradation Test

The CNT-TiO_2 composite-coated diaper was placed on the plate. The ammonia solution was poured onto the plate and set in such a way that the diaper was in contact with the solution. The plate with a spin bar was placed on a magnetic stirrer for homogeneous mixing. It was covered by a Pyrex glass to avoid contact with the outside air. The effectiveness of the composite in eliminating ammonia was also tested in the form of a slurry. The photon source in the experiments was a mercury lamp HPL-N 250W/542 placed on the top of the plate. (We also used 6 units of 10 W/352 nm BLB UV lamps for comparison.) Samples from the ammonia degradation test were taken and tested with the indofenol method using a spectrophotometer at λ = 630 nm, according to SNI 19-7119.1-2005.

2.4. *Candida Albicans* Disinfection Test

This test used a 2cm×2cm diaper that had been prepared and coated with the TiO_2 P25 catalyst. The inoculated sample of *C. albicans* was spread on the diaper and placed on the plate. This test used a simple photoreactor with a lamp source of 1 unit BLB UV lamp 15 W/352 nm. A sample from the disinfection test was taken at several time intervals. The total colony of *C. albicans* was calculated by a total plate count (TPC).

3. RESULTS AND DISCUSSION

3.1. FTIR

FTIR spectra of CNT-TiO_2 is shown in Figure 1. The CNT-TiO_2 composite has a peak that indicates a carbon and TiO_2 bond and all identifiable functional groups. The peaks of the composite at 450 cm^{-1} and 1400 cm^{-1} are consistent with a stretching vibration of Ti-O-Ti bonding, indicating a TiO_2 crystal. In addition, the peaks at 1640 cm^{-1} and 3400 cm^{-1} can be assigned to the bending and stretching vibration of an O-H group, indicating chemical and surface catalyst adsorption of water (Cai et al., 2012). The indication of CNT and titanium bonding is shown by the peak that appears at 1008–1100 cm^{-1}. This peak is not as sharp as that of the normal strong characteristic peak of the Ti-O-C stretch of bonding between CNT and TiO_2 in the composite (Vasconcelos et al., 2011) but unambiguously indicates the existence of the mentioned bond.

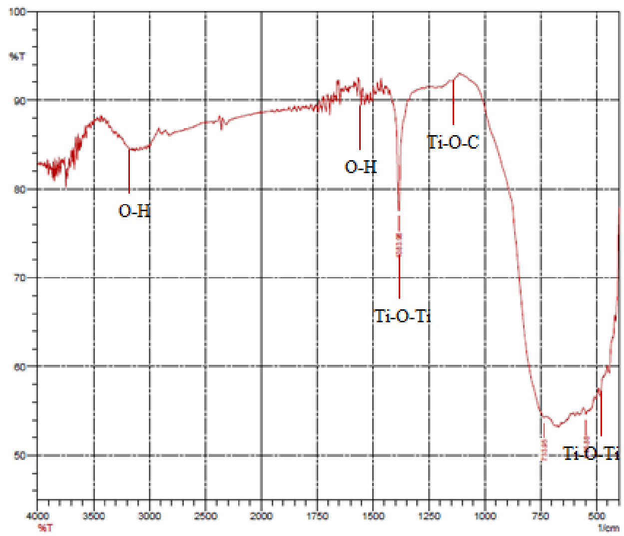

Figure 1 FTIR spectra of the CNT-TiO_2 composite

3.2. FESEM-EDX Characterization

SEM images of the MWCNT, TiO_2 P25, and CNT-TiO_2 composite are shown in Figure 2. Figure 2(a) shows the morphology of the MWCNT, which is clearly visible and allows the calculation of the diameter of the MWCNT, which is about 40–60 nm; most have a diameter above 90 nm. The morphologies of the TiO_2 P25 and the CNT-TiO_2 can be compared in Figure

2(b) and Figure 2(c), respectively. These confirm that a composite has been formed between TiO_2 particles and CNT. There is sufficient CNT and TiO_2 coated on the composite surface.

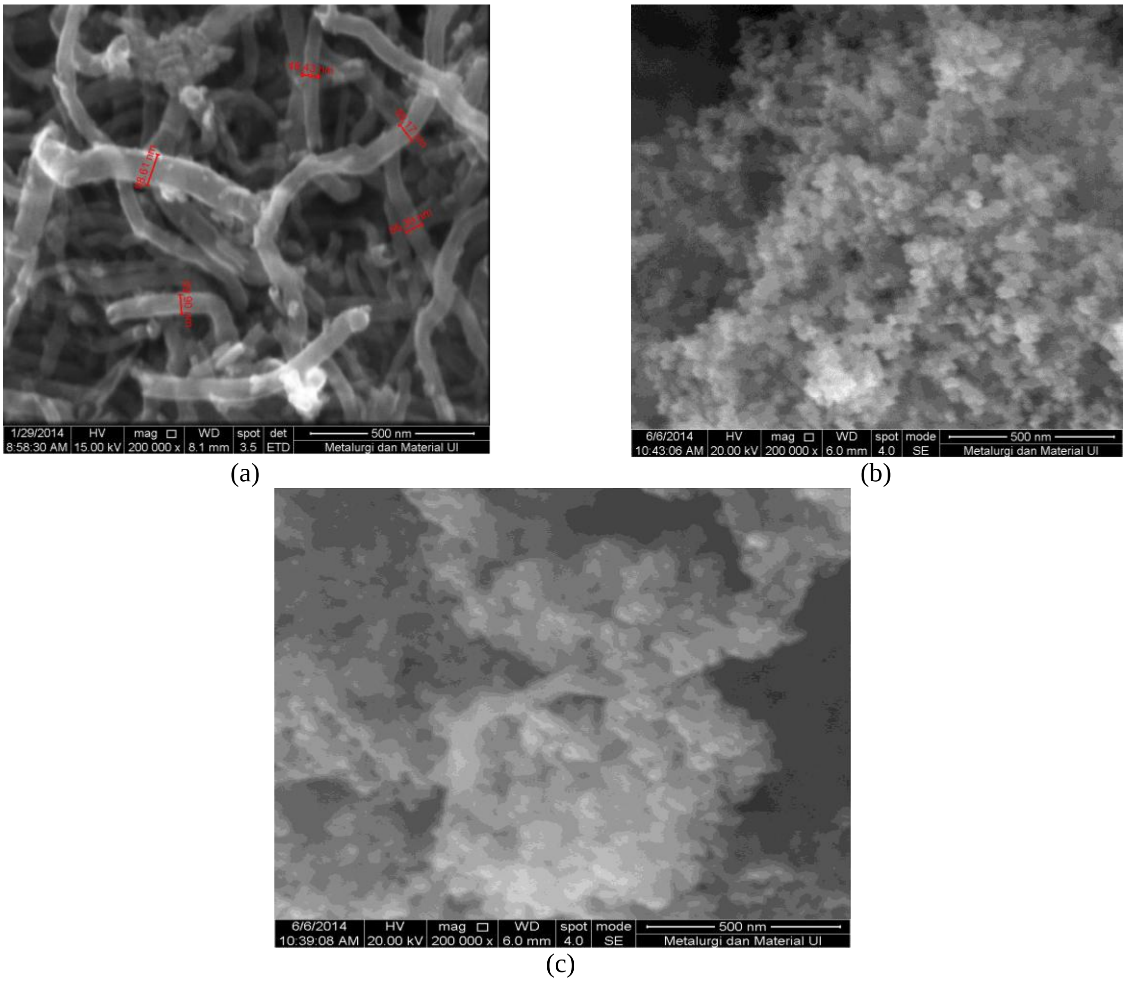

Figure 2 FESEM image of: (a) CNT; (b) TiO_2 P25; (c) CNT-TiO_2 composite

Table 1 shows the EDX results from the best of the CNT-TiO_2 composite. The mass percentage of carbon at the composite sampling sites 1, 2, and 3 are 2.92%, 2.93%, and 2.68%, respectively with an average of 2.84%.

Table 1 EDX results of CNT-TiO_2 composite in each location of the sample

Location	Weight% Component		
	C	O	Ti
1	2.92	40.47	56.61
2	2.93	41.44	55.63
3	2.68	40.34	56.98
Mean	2.84	40.75	56.41

The composition was almost homogeneous for the CNT-TiO_2 composite with 3 wt% CNT. These results indicated that the dispersion of CNT and TiO_2 particles in the mixture was sufficient. This can be achieved during the synthesis of the composites, a series of acid treatments, and the sonication process, which can decrease the aggregation size of the composite and so easily cause dispersion in the mixture.

3.3. XRD

XRD patterns of CNT-TiO_2 and TiO_2 P25 are shown in Figure 3. Obvious carbon diffraction peaks can be observed in the CNT-TiO_2 composite. Furthermore, CNT-TiO_2 has anatase and rutile diffraction peaks that are higher than the peaks from TiO_2 P25. These results may be due to the size of the catalyst crystal. The higher peak of the CNT-TiO_2 composite in several parts of 2θ was caused by an overlapping CNT peak.

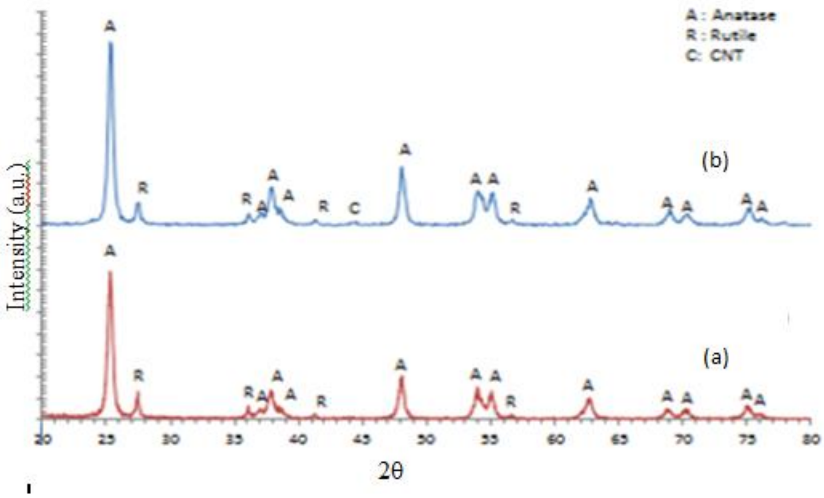

Figure 3 XRD pattern of: (a) TiO_2 P25; (b) CNT-TiO_2

The crystallite size calculated by the Scherrer equation for the CNT-TiO_2 composite and TiO_2 P25 can be seen in Table 2.

Table 2 Mass fraction and size of catalyst crystal of TiO_2 P25 and CNT-TiO_2

Catalyst	Anatase (wt%)	Size of Crystal (nm)		
		Anatase	Rutile	Carbon (CNT)
TiO_2 P25*	79.24	20	23	-
CNT-TiO_2	86.00	18	20	10–30

*(Slamet et al., 2005)

3.4. UV-VIS DRS

Figure 4 shows the UV-Vis DRS characterization of the CNT-TiO_2 composites and TiO_2 P25. By extrapolating the results from the straight line toward the *x*-axis, the CNT-TiO_2 composite response to visible light is shown to be greater than that of TiO_2 P25. The CNT-TiO_2 composite can respond to photons with a wavelength in the visible light range (light with a low intensity of photons).

Figure 4 (b) shows that the CNT-TiO_2 composite and TiO_2 P25 catalyst successively obtained a band gap of 2.8 eV and 3.25 eV, respectively. This result shows that the presence of CNT in the composite to form Ti-O-C bonds improves the responsiveness of the composite to visible light (i.e., the band gap of the composite is lower than that of TiO_2 P25).

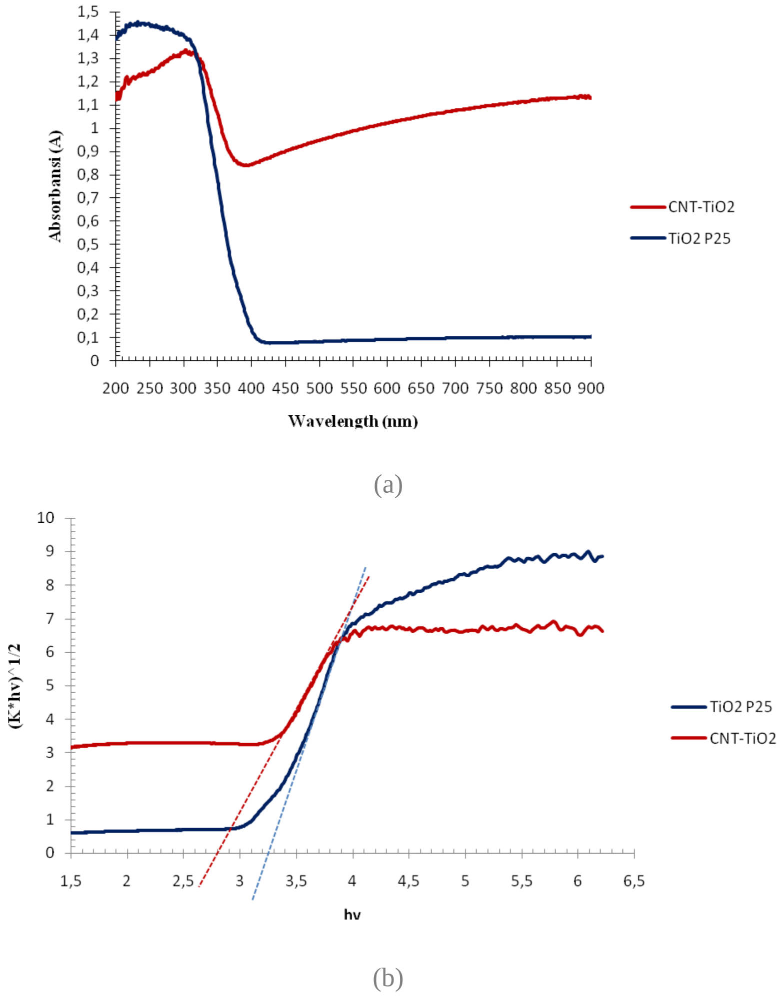

Figure 4 Characterization of: (a) absorbance of UV-VIS DRS; (b) band gap of CNT-TiO_2 and TiO_2 P25

3.5. Ammonia Degradation Test

3.5.1. Effect of light condition (evaporator effect)

In this experiment, ammonia was eliminated by photocatalytic degradation through oxidation reaction (Altomare et al., 2012). Figure 5 shows the evaporation effect in the ammonia degradation test.

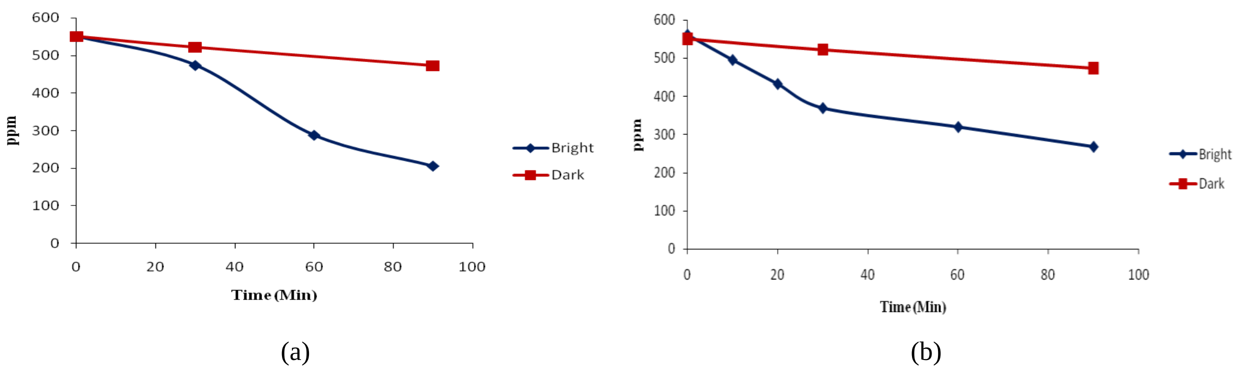

Figure 5 Ammonia degradation test using: (a) 1 unit of a mercury lamp at 250 W; (b) 6 units of a UV lamp at 10 W

These tests use two types of lamps: 6 units of a 10-W UV lamp and 1 unit of a 250-W mercury lamp; results were compared to results without light. This process occurs because the ammonia in the water will easily evaporate with increasing temperature and pH of the solution. Ammonia elimination using mercury lamps at 45°C is about 267 ppm at 90 minutes, while ammonia elimination by UV lamp at 27°C leads to reduced ammonia by around 204 ppm at 90 minutes. The ammonia, which is dissolved in water, is vaporized to NH_3 gas and partially ionized to NH_4^+ ions. The ammonium dissociation constant (Kb) is slightly increased with increasing solution temperature.

3.5.2. Effect of acid treatment

Results of the ammonia degradation test using CNT-TiO_2 with CNT from the acid treatment process is shown in Figure 6. CNT-TiO_2 is shown to be the best composite to eliminate ammonia. This is because the CNT-TiO_2 composite has a combined adsorption–photocatalytic effect. The effectiveness of the composite is therefore greater than TiO_2 alone in ammonia degradation. CNTs have been shown to be high co-adsorbents with pores and a relatively large surface area (40–300 m^2/g) (Sampaio et al., 2011). In addition to being a co-absorbent and electron trapper, CNT as a pair of TiO_2 in a composite can also serve as a dispersant and photosensitizer. The greatest characteristic of a composite with acid treatment on a CNT is the negatively charged groups, such as COO^- and OH^-. TiO_2 in acid conditions has a positive potential value; therefore, a mixture of CNT-TiO_2 in acid conditions will produce a composite with strong chemical bonds.

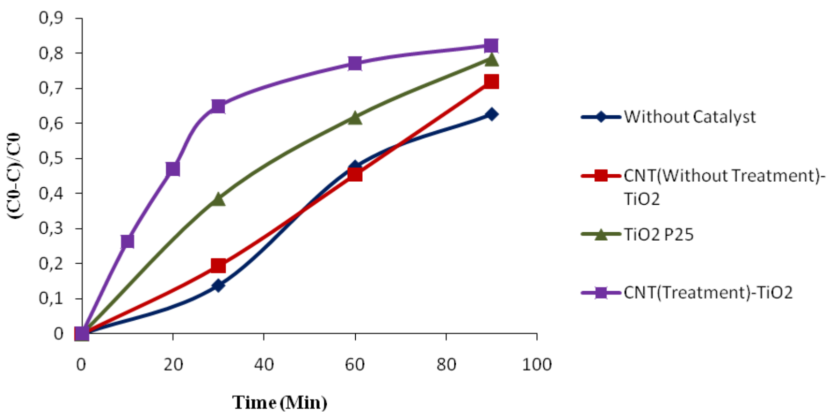

Figure 6 Acid treatment effect of CNT in the ammonia degradation test

3.5.3. Effect of CNT loading

Figure 7 shows that the optimum composition is a composite with a CNT mass of 1–3%. This can occur because these CNT loadings give TiO_2, as a photocatalyst, maximum degradation in the ammonia test. This is supported by the absorbent, electron trapper, dispersant, and photosensitizer properties from the CNT. However, a CNT greater than the optimum loading will lock a portion of the porosity of the TiO_2 and may block the photon path of the photocatalyst, thus hindering the photocatalytic process. This effect is known as shading. A composite with loadings of 0% and 100% of CNT-TiO_2 is less effective in the degradation of ammonia.

3.5.4. Effect of pH in composite synthesis

The optimum pH for synthesizing the CNT-TiO_2 composite to give an optimum performance in eliminating ammonia is pH 1, as shown in Figure 8. As the pH of the mixture decreased, a better composite was formed and pollutant removal was more effective.

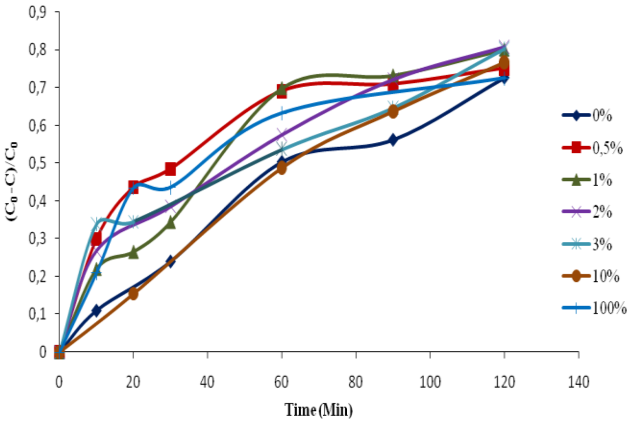

Figure 7 Effect of CNT loading in the ammonia degradation test

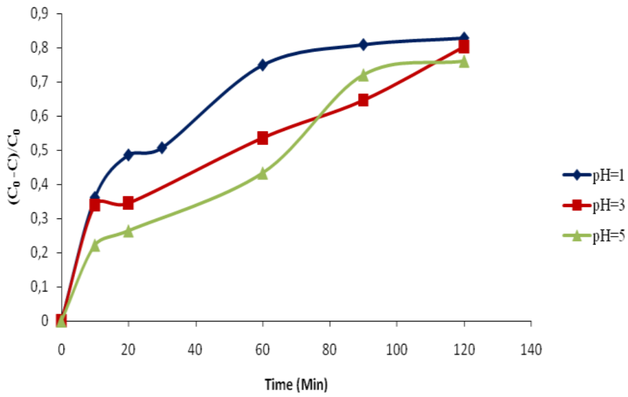

Figure 8 Effect of pH on composite synthesis in the ammonia degradation test

Table 3 EDX results of CNT-TiO_2 at each pH of the synthesized composite

pH	Weight% Component		
	C	O	Ti
1	2.84	40.75	56.41
3	2.61	39.69	57.70
5	2.58	35.08	62.34

Based on the EDX data in Table 3, the composition of carbon (CNT) in the composite at pH 1 was greater than the other composites. The initial composition of the CNT in this composite before synthesis was 5%. The composite was synthesized through a precipitation process, and the part that did not precipitate was separated and then dried as the CNT-TiO_2 composite.

3.5.5. Flexibility of composite to visible light in the ammonia degradation test

Figure 9 shows that the composite with the optimum composition was not only active under UV light but was also active in eliminating ammonia under visible light. This testing reached the greatest efficiency, with 91% degradation, by 1 unit of a mercury lamp HPL-N at 250 W, showing that the optimal composite was responsive to visible light although it was also influenced by evaporation and light intensity. However, light intensity will influence the effectiveness of the catalyst when the photon energy band from the lamp is the same as or greater than the band gap of the catalyst. If the photon energy band is less than the band gap of the catalyst, the level of intensity will not be sufficient to influence the result. Therefore, a lower band gap of CNT-TiO_2 is the main reason why the ammonia degradation test using the 250-W mercury lamp is effective.

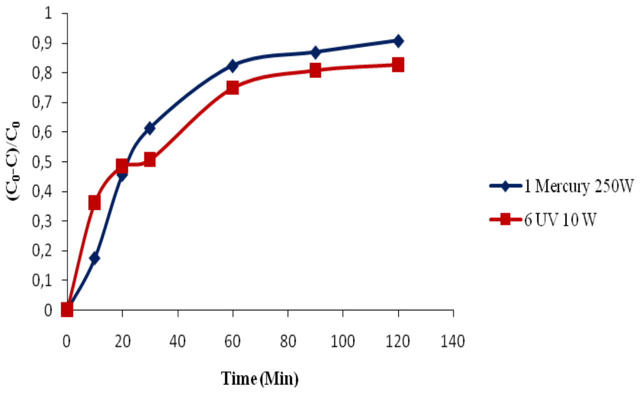

Figure 9 Ammonia degradation test with the optimal composite under UV and visible light

3.6. Disinfection of *Candida albicans*

This test showed the decrease in the *C. albicans* colonies from 9.20×10^7 to 2.01×10^6 CFU or 98% disinfection within 2 hours. Figure 10 shows the results of disinfection. The maximum level of *Candida* that is safe is less than 10^3 CFU. In fact, the number that was achieved by the experiment was above the minimum safe level. However, the disinfection trend was decreasing. To obtain the minimum safe level, the diaper should be tested after more than 2 hours. Furthermore, the number of colonies of *C. albicans* tested was the maximum colonies in the worst case of candiasis disease, whereas a common case of candiasis could be caused by 10^3–10^5 CFU. The common number of colonies can be disinfected in only 2 hours based on the results of this experiment. Disinfection by TiO_2 P25 was supported by the photocatalytic process (the presence of the catalyst and UV light), while any disinfection without the presence of catalyst is due to UV light only. UV light has an effect in this test because it can disinfect microorganisms, including yeast. However, UV light that is used in testing is UV-A, which does not significantly affect the result.

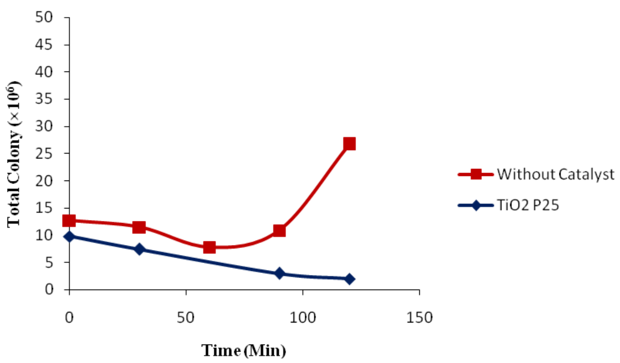

Figure 10 Ammonia degradation test with the optimal composite under UV and visible light

Disinfection of *C. albicans* by TiO_2 is due to the redox reaction in the membrane of yeast by hydroxyl radicals and $\cdot O_2^-$ after TiO_2 is activated. TiO_2 can damage the cell walls of microorganisms and the cytoplasm membrane (Malato & Ibanez, 2006). Hydroxyl radicals and

$\cdot O_2^-$ are formed through the hole and electron. Hydroxyl radicals and $\cdot O_2^-$ will attack the outer membrane of *C. albicans* until the cell membrane shatters.

4. CONCLUSION

Diaper that had been contaminated by ammonia and *C. albicans* was able to be cleaned up to minimum standard to prevent odor and diaper rash in the presence of the synthesized CNT-TiO_2 composite. The optimum composition of the composite was found to be 1–3 wt% of CNT and 97–99 wt% of TiO_2 and reached maximum degradation by using a mercury lamp. Acid treatment of the CNT-TiO_2 composite at pH 1 resulted in the best composite performance. Characterization showed that the CNT-TiO_2 composite has a high crystalline and low band gap. Ammonia and *C. albicans* with 0.1 g/ml of the optimum composite can be removed and disinfected up to 91% and 98%, respectively, in two hours.

5. ACKNOWLEDGEMENT

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