The role of surfactant to enhance photocatalyst performance on phenol degradation in TiO$_2$-CNT composite-modified CNT (Cetyltrimethylammonium bromide)

D Heltina$^1$, U Avisa$^1$ and M I Fermi$^1$

$^1$Riau University, Department of Chemical Engineering, Pekanbaru, 28293, Riau, Indonesia

Corresponding author: desi.heltina@lecturer.unri.ac.id

Abstract. The TiO$_2$-CNT composite – modified CNT (Cetyltrimethylammonium bromide) photocatalyst material was successfully prepared. The composites material was characterized by Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD), Fourier Transform Infrared absorption spectroscopy (FTIR), and Brunauer Emmet Teller (BET). The TiO$_2$-CNT composite- modification CNT (Cetyltrimethylammonium bromide) formation obtained are discussed in detail. The highest performance effectiveness of photocatalyst material composites for degrading phenol was obtained on phenol concentration 10 mg/L and degradation temperature at 50°C was 98.74%.

1. Introduction
Phenol is a dangerous type of industrial waste. Phenol can be found in wastes from various industries such as polymer, plastics, pulp and paper, and textile industries [1,2]. The past few years photocatalysis process has become the choice in degrading waste compounds such as phenol because it is a process that can degrade phenol to CO$_2$ and H$_2$O [3,4].

The photocatalyst material which is widely used for the photocatalysis process is titanium dioxide (TiO$_2$). Titanium dioxide (TiO$_2$) has a band gap energy greater than 3 eV (anatase = 3.2 eV is equivalent to 380 nm and rutile = 3.1 eV is equivalent to 410 nm) so it makes TiO$_2$ is active when exposed to UV light [5]. In the photocatalyst material oxidation and reduction processes occur which results in the hole reacting with H$_2$O contained in solution to form hydroxyl radicals (•OH). This hydroxyl radical is a strong oxidizer that can degrade organic compounds to CO$_2$, H$_2$O and halide ions. Electrons on the surface of TiO$_2$ can react to form superoxide radicals (•O$_2^-$) which can also degrade organic compounds in solution [6]. But the effectiveness of the performance of TiO$_2$ is hampered by the rate recombination between electron pairs and holes [7].

Photocatalytic activity is increased when the use of TiO$_2$-CNT composites in the process of photocatalysis [8]. When TiO$_2$ binds CNT to form a composite, CNT encourages the transfer of electrons from the TiO$_2$ conduction band to the surface of the CNT. So the CNT receives and stores photogeneration electrons and inhibits the recombination of electron and holes. These electrons can be transferred to other electron acceptors such as oxygen molecules to form reactive oxygen species (O$_2$, H$_2$O$_2$, and •OH) that can degrade organic pollutants [9].
Studies show that there are weaknesses in TiO$_2$-CNT composites such as low CNT solubility levels. Cetyltrimethylammonium bromide (CTAB) is a type of cationic surfactant that is widely used to increase the stability of CNT in solution [10]. The surface of the CNT is hydrophobic. Addition of surfactant is a way to increase stable dispersion between CNT and TiO$_2$. Surfactants have a molecular structure consisting of hydrophilic and hydrophobic groups. Hydrophilic groups can be well dispersed in water and organic solvents, while hydrophobic groups will form bonds with CNT [11].

The purposes of this research are to synthesize and obtain the characterization of TiO$_2$-CNT composites – modified CNT(Cetyltrimethylammonium bromide) and obtain the performance effectiveness in degrading phenol.

2. Material and methods
The synthesized of TiO$_2$-CNT composite-modified CNT (CTAB) were carried out with two main processes, which were surface modification of CNT in the CTAB surfactant and then compiled it with TiO$_2$. The performance of TiO$_2$-CNT composite-modified CNT (CTAB) was tested for phenol degradation.

2.1. Materials
TiO$_2$ (P25), CNT for the research was multi walled carbon nanotube (MWCNT) type purchased from Dong Yang (HK) Int'l Group Limited of diameter 10-30 nm, length of 5-15 μm, and purity of 99%, Cetyltrimethylammonium bromide (CTAB), 0.1 M HNO$_3$ and aquades.

2.2. CNT Modification with CTAB (Cetyltrimethylammonium bromide) Surfactant
1 gram of carbon nanotube (CNT) was added with CTAB surfactant of 0.5 gram in 100 mL aquades. Solution was then sonicated for 1 hour. Then solution was dried.

2.3. Synthesis of TiO$_2$-CNT Composite -Modified CNT (Cetyltrimethylammonium bromide)
0.015 gram of CNT(CTAB) was dissolved in 100 ml aquades. The mixture was sonicated for 30 minutes. Then re-sonication for 30 minutes with the addition of 1 gram of TiO$_2$. The pH of mixture was adjusted until pH is 3 by added 0.1 M HNO$_3$ and after that the mixture stirred by using magnetic stirrer 300 rpm for 3 hours. The mixture then dried in temperature of 100-110°C for 2 hours. Sample calcined at a high temperature 400°C for 2 hours in a nitrogen atmosphere.

2.4. Performance test of TiO$_2$-CNT composite-modified CNT (CTAB) for phenol degradation.
TiO$_2$-CNT composite-modified CNT (CTAB) each of 0.3 gram was put into 300 mL of phenol liquid of 10 ppm, 20 ppm and 30 ppm. The experiment was conducted for 270 minutes (4.5 hour), in which first 30 minutes was conducted without light (light off) and next 240 minutes the photodegradation using a 60 watt UV lamp as photon source (light on) was conducted and degradation temperatures of 30°C, 40°C, and 50°C. Photocatalyst used for the process was 0.3 gram powder and continuously stirred during experiment in order to make photocatalyst particles and phenol distributed evenly in sample solution. Quantitative result of degrade phenol was acquired by using UV-Vis Spectrophotometer in accordance with procedure on SNI 06-6989.21-2004.

2.5. Characteristic
Sample was characterized by using SEM, BET, FT-IR , XRD, and UV-vis spectroscopy.

3. Results and discussion
Figure 1 shows SEM images of the TiO$_2$-CNT composite- modified CNT (CTAB). These look TiO$_2$ particles are well distribute among the CNT and there are some particles of TiO$_2$ gathered together to form small groups. The spread of CNT is not clearly visible because of the small amount of CNT than TiO$_2$. Even distribution of particles showed that the synthesis of TiO$_2$-CNT composite-modified CNT (CTAB) was successful.
Figure 1. SEM images of TiO$_2$-CNT composite–modified CNT (CTAB).

The BET surface area of the TiO$_2$, CNT, TiO$_2$-CNT, TiO$_2$-CNT composite –modified CNT (Cetyltrimethylammonium bromide) composite is shown in table 1. Based on table 1 it can be seen that an increase in the surface area of TiO$_2$ photocatalysts after the addition of CNT. This can be seen from research by Miandoab and Fatemi [12] where an increase in the surface area of TiO$_2$-CNT is 62.3 m$^2$/g. Increased surface area shows that CNT can affect the surface area of photocatalysts. This statement is in accordance with the results of research Huang et al.[8] that CNT can provide greater specific surface area in photocatalysts. In this research, the surface area of photocatalyst is 84.75 m$^2$/g which is bigger than the research conducted by Miandoab and Fatemi [12]. Surface modification of CNT with CTAB surfactant resulted in an increase in surface area on TiO$_2$-CNT composites. According to Manilo et al. [10] CTAB surfactant is one type of cationic surfactant that is widely used to improve the stability of CNT in solution, so that it can help CNT dispersion in solution. so that this can be proven by increasing the surface area of the TiO$_2$-CNT composite (Cetyltrimethylammonium bromide) obtained.

| Sample                                | Surface Area (m$^2$/g) |
|---------------------------------------|------------------------|
| aTiO$_2$ P25                          | 53.6                   |
| bCNT                                  | 200                    |
| cTiO$_2$-CNT                          | 62.3                   |
| TiO$_2$-CNT–modified CNT (CTAB)       | 84.75                  |

aSlamet et al. [13]  
bHeltina et al. [14]  
cMiandoab and Fatemi [12]

The FTIR spectra of TiO$_2$-CNT composite-modified CNT (CTAB) is given in figure 2. Peaks at 3188.47 cm$^{-1}$ and 3853.94 cm$^{-1}$ indicates the presence of the –OH groups. The –OH group indicates that water molecules are adsorbed on the surface of the photocatalyst [15]. According to Linsebigler et al.[16] -OH groups in water molecules can act as electron donors from holes formed by the induction of light and will produce hydroxyl radicals (•OH) which are very helpful in increasing photocatalytic activity. At wavelengths of 2953.14 cm$^{-1}$ it is a C-H bond from the surface of the CNT [17]. At a wavelength of 2361.94 cm$^{-1}$ it is a C-C bond [18]. The bonds C = O and C = C are present at wavelengths of 1549.87 cm$^{-1}$ and 1647.28 cm$^{-1}$[19]. Ti-O-Ti and Ti-O-C bonds are found at wavelengths below 798 cm$^{-1}$ [20]. According to Lee et al.[21] the formation of Ti-O-C bonds between
TiO$_2$ and CNT causes close contact between TiO$_2$ and CNT thus offering an efficient route for electron transfer from the TiO$_2$ conduction band to the surface of the CNT.

**Figure 2.** FTIR images of TiO$_2$-CNT composite–modified CNT (CTAB).

The crystal structure of the TiO$_2$-CNT composite-modified CNT (CTAB) can be investigated using the XRD pattern as shown in figure 3. The diffraction peaks at 25.29°, 48.03°, 37.83°, 53.94°, 55.05°, 62.71°, 68.88°, 70.22°, and 75.08° correspond to the (101), (200), (004), (105), (211), (204), (116), (220) and (215) reflections of anatase, respectively. The peaks at 2θ values of 27.42° is related to rutile (110). But besides these peaks there are also peaks centered on 2θ; 26° which indicates the presence of carbon structures (002) that overlaps with the anatase (101) crystal peaks [8].

**Figure 3.** XRD patterns of TiO$_2$-CNT composite-modified CNT (CTAB).

From the XRD analysis the crystal size of the TiO$_2$-CNT composite-modified CNT (CTAB) was obtained using the Scherer Equation as inequation (1).

\[
D = \frac{0.9 \lambda}{\beta \cos \theta}
\]  

(1)

In order to obtain the crystal size and crystal fraction of the TiO$_2$-carbon nanotube (Cetyltrimethylammonium bromide) composites shown in table 2. And it is known that the mixture of
anatase and rutile crystals has a synergistic effect and increased photocatalytic activity compared to pure phase [22].

**Table 2.** Size and crystalline fraction of TiO$_2$-CNT composite–modified CNT (CTAB).

|                  | Anatase | Rutile |
|------------------|---------|--------|
| Crystal size (nm)| 17.73   | 23.72  |
| Crystal fraction (%)| 14.22  | 85.78  |

The effect of phenol concentration on the performance of photocatalyst material to degrade phenol was studied. The research variables were carried out with different initial phenol concentrations of 10, 20 and 30 mg/L, respectively.

**Figure 4.** Effect of phenol concentration on the performance of composites to degrade phenols.

Figure 4 shows that the percentage degradation of phenol has decreased with increase in initial concentration of phenol. It was found that 98.74% degradation of phenol occurred within 240 minutes with degradation temperature 30°C. At lower concentrations it can be observed that high rates of degradation. the use of a fixed amount of catalyst with increasing phenol concentration makes the hydroxyl radical (•OH) produced on the surface of the catalyst also constant while the amount of phenol that needs to be degraded increases so that the amount of hydroxyl radical (•OH) that is available is unable to completely degrade phenol. In addition, this opinion is also supported by the results of research Chong et al.[23] that high phenol concentrations can reduce the absorption of photons by photocatalyst particles, because increasing phenol molecules cover the surface of photocatalysts thereby reducing the activity of photocatalysts which causes a decrease in the performance of photocatalysts.

The effect of temperature degradation on the performance of photocatalyst material to decrease phenol was also studied. One of the factors that also affects photocatalytic degradation is the temperature of degradation. The experiments carried out with variations in the degradation temperature of 30, 40 and 50°C, respectively. Based on figure 5, the percentage increase in degradation occurs with increasing temperature degradation used. It can be seen that at the initial concentration of 10 ppm phenol there was an increase in the percentage of degradation from temperatures 30°C, 40°C and 50°C.
Figure 5. Effect of temperature on the performance of composites to degrade phenols.

According to Kumar and Pandey [24], rising temperatures result in increased interactions that occur between phenol molecules and the surface of the photocatalyst. This opinion is also supported by the research of Mamba et al. [25] that the best temperature range for the photocatalysis process is 20°C-80°C. An increase in reaction temperature generally increases photocatalysis activity but when the degradation temperature is above 80°C it encourages recombination of the photocatalyst material and a further decrease in temperature to 0°C will increase activation energy. Therefore the degradation temperature of 20°C-80°C is the best range for the degradation process to occur [24].

Figure 6 below shows the performance of photocatalysts in degrading phenols from TiO₂, TiO₂-CNT composite-modified CNT (CTAB) and CNT with phenol degradation percentage of 89%, 98.74% and 29% respectively. Performance TiO₂-CNT composite-modified CNT (CTAB) has a higher photocatalyst performance than other materials. This degradation result is also supported by the results of SEM characterization on composites characterized by the presence of well distributed TiO₂ particles between CNT and also the presence of Ti-O-C bonds in the FTIR characterization results indicating close contact between TiO₂ and CNT thus offering an efficient route for electron transfer from the TiO₂ conduction band to the surface of the CNT [21].

Figure 6. Effectivity of performance of TiO₂-CNT composite – modified CNT (CTAB) to phenol degradation.
4. Conclusion

The TiO$_2$–CNT composite–modified CNT (Cetyltrimethylammonium bromide) photocatalyst material has been successfully synthesized. Effectivity of performance of photocatalyst material composite was influenced by crystallinity, morphology and function group. The highest performance effectiveness of photocatalyst material composites for degrading phenol was obtained on phenol concentration 10 mg/L and degradation temperature at 50°C was 98.74%.

Acknowledgement

The authors would like to thank DRPM Universitas Riau and Directorate General of Higher Education (DGHE) Indonesian Ministry of National Education for the financial support of this research (Hibah) Penelitian Dasar, no. 395/UN.19.5.1.3/PT.01.03/2020.

References

[1] Dargahi A, Mohammadi M, Amirian F, Karami A and Almasi A 2017 Phenol removal from oil refinery wastewater using anaerobic stabilization pond modeling and process optimization using response surface methodology (RSM) Desalin. Water Treat.87 199–208
[2] Pradeep N V., Anupama S, Navya K, Shalini H N, Idris M and Hampannavar U S 2015 Biological removal of phenol from wastewaters: a mini review Appl. Water Sci.5 105–12
[3] Liwei D 2007 City environment art and sustainable development Chinese J. Popul. Resour. Environ.5 63–6
[4] Tao Y, Cheng Z L, Ting K E and Yin X J 2013 Photocatalytic Degradation of Phenol Using a Nanocatalyst: The Mechanism and Kinetics J. Catal.2013 1–6
[5] Hermawan P, Pranowo H D and Kartini I 2011 Physical Characterization Of Ni(Ii) Doped TiO$_2$ Nanocrystal By Sol-Gel Process Indones. J. Chem.11 135–9
[6] Hoffmann M R, Martin S T, Choi W and Bahnemann D W 1995 Environmental Applications of Semiconductor Photocatalysis Chem. Rev.95 69–96
[7] Tan T L, Lai C W, Hong S L and Rashid S A 2018 New insights into the photocatalytic endocrine disruptors dimethyl phathalate esters degradation by UV/MWCNTs-TiO2 nanocomposites J. Photochem. Photobiol. A Chem.364 177–89
[8] Huang L, Chan Q, Wu X, Wang H and Liu Y 2012 The simultaneous photocatalytic degradation of phenol and reduction of Cr(VI) by TiO2/CNTs J. Ind. Eng. Chem.18 574–80
[9] Liu X, Wang M, Zhang S and Pan B 2013 Application potential of carbon nanotubes in water treatment: A review J. Environ. Sci. (China)25 1263–80
[10] Manilo M V., Lebovka N and Barany S 2017 Combined effect of cetyltrimethylammonium brome and platelet on colloidal stability of carbon nanotubes in aqueous suspensions J. Mol. Liq.235 104–10
[11] Heltina D 2017 Modification of Carbon Nanotube for Synthesis of Titania Nanotube (Tint)-Carbon Nanotube (Cnt) Composite J. Energy, Mech. Mater. Manuf. Eng.1 29–35
[12] Sorooodan Miandoab E and Fatemi S 2015 Upgrading TiO2 Photoactivity under Visible Light by Synthesis of MWCNT/TiO2 Nanocomposite Int. J. Nanosci. Nanotechnol.11 1–12
[13] Slamet A R and W 2005 Pengolahan Limbah Cr(Vi) Dan Fenol Dengan Fotokatalis Serbuk Tio 2 Dan CuO/Tio$_2$-Prosiding SNTPK Jakarta
[14] Heltina D, Wulan P P D K and Slamet 2015 Synthesis and characterization of titania nanotube-carbon nanotube composite for degradation of phenol Int. J. Technol.6 1137–45
[15] Bao N, Li Y, Wei Z, Yin G and Niu J 2011 Adsorption of dyes on hierarchical mesoporous TiO2 fibers and its enhanced photocatalytic properties J. Phys. Chem. C115 5708–19
[16] Linsebigler A L, Lu G and Yates J T 1995 Photocatalysis on TiO2 Surfaces: Principles, Mechanisms, and Selected Results Chem. Rev.95 735–58
[17] Askari M B, Tavakoli Banizi Z, Seifi M, Bagheri Dehaghi S and Veisi P 2017 Synthesis of TiO2 nanoparticles and decorated multi-wall carbon nanotube (MWCNT) with anatase TiO2 nanoparticles and study of optical properties and structural characterization of
TiO2/MWCNT nanocomposite *Optik (Stuttg).* 149 447–54

[18] Marques Neto J O, Bellato C R, De Souza C H F, Da Silva R C and Rocha P A 2017 Synthesis, characterization and enhanced photocatalytic activity of iron oxide/carbon nanotube/Ag-doped TiO2 nanocomposites *J. Braz. Chem. Soc.* 28 2301–12

[19] Saleh T A, Siddiqui M N and Al-Arfaj A A 2014 Synthesis of multiwalled carbon nanotubes-titania nanomaterial for desulfurization of model fuel *J. Nanomater.* 2014

[20] X. Pan, Y. Zhao, S. Liu, C. L. Korzeniewski S W and Z F 2012 Supporting Information Supporting Information *ACS Appl. Mater. Interfaces* 2 1–5

[21] Lee D H, Park J G, Kyoung J C, Choi H J and Kim D W 2008 Preparation of brookite-type TiO2/carbon nanocomposite electrodes for application to Li ion batteries *Eur. J. Inorg. Chem.* 878–82

[22] Scanlon D O, Dunnill C W, Buckeridge J, Shevlin S A, Logsdail A J, Woodley S M, Catlow C R A, Powell M J, Palgrave R G, Parkin I P, Watson G W, Keal T W, Sherwood P, Walsh A and Sokol A A 2013 Band alignment of rutile and anatase TiO2 *Nat. Mater.* 12 798–801

[23] Chong M N, Jin B, Chow C W K and Saint C 2010 Recent developments in photocatalytic water treatment technology: A review *Water Res.* 44 2997–3027

[24] Kumar A 2017 A Review on the Factors Affecting the Photocatalytic Degradation of Hazardous Materials *Mater. Sci. Eng. Int. J.* 1

[25] Mamba G, Mamo M A, Mbianda X Y and Mishra A K 2014 Nd,N,S-TiO2 decorated on reduced graphene oxide for a visible light active photocatalyst for dye degradation: Comparison to Its MWCNT/Nd,N,S-TiO2 Analogue *Ind. Eng. Chem. Res.* 53 14329–38