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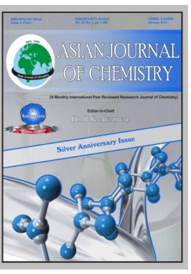

Wastewater Treatment by CNT/TiO_2 Composites Prepared from Multi-Walled Carbon Nanotubes with Different Organo-Titanium Precursors

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We prepared CNT/TiO_2 composites by using pre-oxidized multi-walled carbon nanotubes with different titanium alkoxide precursors in benzene solvent. The composites were comprehensively characterized by Brauer-Emett-Teller surface area, transmission electron microscopy, X-ray diffraction and energy dispersive X-ray analysis. Furthermore, we used the prepared CNT/TiO_2 composites to decompose the piggery waste under UV irradiation. The decomposition effect was analyzed by using the chemical oxygen demand method, FT-IR spectra, absorbance and total organic carbon. According to the results, after UV irradiation for 300 min, the chemical oxygen demand value was decreased 50 % and the organic compounds in piggery waste were degraded to other matters.

Key Words: Multi-walled carbon nanotubes, TEM, Chemical oxygen demand, Piggery waste.

INTRODUCTION

One of the main problems related to the environmental protection is the adequate management and treatment of piggery wastes. Pig farms with hundreds to several thousands of animals are in operation in many countries without adequate systems for waste treatment and disposal. Manure, urine and food remains are washed out from the cages with volumes of water not adequately controlled causing a great variation in the volume and concentration of the effluents. This situation has caused the failure of conventional wastewater treatment plants[1].

Oxygen demand is an important parameter for assessing the concentration of organic contaminants in water resources. Since the degradation of organic compounds requires oxygen, their concentrations can be estimated by the quantity of required oxygen[2,3]. Chemical oxygen demand (COD) is the main index used to assess organic pollution in aqueous systems[4]. In recent years, a great deal of effort has been devoted to the development of rapid, sensitive and environmentally friendly methods for the determination of chemical oxygen demand. The photocatalysis is one of the techniques, which is called advanced oxidation processes. Advanced oxidation processes offer a highly reactive, non-specific oxidant namely hydroxyl radical ($^{\cdot}OH$) which is capable of destroying wide range of organic pollutants non-selectively and quickly in water and wastewater[5-9]. These processes can completely degrade the organic pollutants into harmless inorganic substances such as CO_2 and H_2O under moderate conditions.

As a good support for nanomaterials, multi-walled carbon nanotube (MWCNT) has been widely investigated due to their high mechanical[10] and chemical[11] stability and their mesoporous character which favours the diffusion of reacting species. Moreover, TiO_2/MWCNT composites have gained a lot of attentions, which could create many active sites for the photocatalytic degradation. Different techniques have already been used to obtain TiO_2/MWCNT composites. Jitianu and his co-workers coated multi-walled carbon nanotube with anatase by using a sol-gel method using classical alkoxides as precursors[12]; Wang *et al.*[13] prepared TiO_2/MWCNT composites with multi-walled carbon nanotube embedded in TiO_2 nanoparticles by a modified sol-gel method and investigated their activity in photodegradation of phenol under irradiation of visible light. In our previous studies[14-17], we also prepared CNT/TiO_2 composites with multi-walled carbon nanotubes which pre-oxidized with *m*-chloroperbenzoic acid and different titanium alkoxide precursors and investigated their activity in photodegradation of methylene blue solution under irradiation of UV light. And it had been indicated that the CNT/TiO_2 composites had more efficiency of methylene blue degradation than pure TiO_2, due to multi-walled carbon nanotube could accept the electron (e^-) from the UV irradiation and transfer to the conduction band of TiO_2 thus increasing the amount of electron and hole for creating the O_2^- (superoxide radical ion) and OH· (hydroxyl radical).

We use the sol-gel method to prepare the CNT/TiO_2 composites. Three kinds of classical alkoxides: titanium(IV) *n*-butoxide (TNB, $Ti\{OC(CH_3)_3\}_4$), titanium(IV) *iso*propoxide (TIP, $Ti\{OCH(CH_3)_2\}_4$) and titanium(IV) propoxide (TPP, $Ti(OCH_2CH_2CH_3)_4$) as precursors were used to form TiO_2 and multi-walled carbon nanotube was pre-oxidized with *m*-chloroperbenzoic acid, resulting in CNT/TiO_2 composites. The resultant CNT/TiO_2 composites were characterized by different techniques including Brunauer-Emmett-Teller (BET) surface area measurement, transmission electron microscopy, X-ray diffraction and energy dispersive X-ray analysis (EDX). The prepared $MWCNT/TiO_2$ composites were used to degrade the piggery waste under the UV light irradiation. To investigate the degradation effect of piggery waste by CNT/TiO_2 composites, the chemical oxygen demand, fourier transform infrared (FT-IR) spectroscopy, absorbance and total organic carbon before and after photodegradation by CNT/TiO_2 composites were analyzed.

EXPERIMENTAL

Crystalline multi-walled carbon nanotube (purity, 95.9 wt. %; diameter: -20 nm; length: -5 μm) powder was obtained from Carbon Nano-material Technology Co. Ltd., Korea. The titanium(IV) *n*-butoxide (99 %), titanium(IV) *iso*propoxide (97 %) and titanium(IV) propoxide (98 %) as titanium alkoxide precursors to form the TiO_2 were purchased from acros organics (New Jersey, USA), Kanto Chemical Company (Tokyo, Japan) and Aldrich Chemical Company, respectively. For the oxidization, the surface of multi-walled carbon nanotube, *m*-chloroperbenzoic acid, as the oxidizing agent, was purchased from Acros Organics, New Jersey, USA. Benzene (99.5 %) was used as the organic solvent purchased from Samchun Pure Chemical Co, Ltd., Korea.

Synthesis and characterization of CNT/TIO_2 composites: To prepare the oxidizing agent, 0.96 g *m*-chloroperbenzoic acid was melted in 60 mL benzene. Then 0.2 g multi-walled carbon nanotubes was put into the oxidizing agent, refluxed at 353 K for 6 h until the solid precipitates were formed and dried at 363 K. Titanium alkoxide precursors were dissolved separately in benzene by a ratio of 50:50. The solution was stirred magnetically for 0.5 h to obtain titanium alkoxide precursor/benzene solution. Subsequently, the pre-oxidized multi-walled carbon nanotubes were introduced into the titanium alkoxide precursors/benzene solution. The mixtures were loosely covered and kept stirring by magnet at 343 K for 5 h, until a homogenous multi-walled carbon nanotubes-contained gel formed. The gel was heat treated at 973 K for 1 h with a heating rate of 279 K/min to obtain CNT/TiO_2 composite catalysts. By changing the titanium alkoxide precurors, different samples were obtained. The preparation condition and code of samples were listed in Table-1. BET surface area was measured using a quantachrome surface area analyzer (MONOSORB, USA). SEM (JSM-5200 JOEL, Japan) and transmission electron microscopy (TEM, JEOL, JEM-2010, Japan) were used to observe the surface state and structure of the CNT/TiO_2 composites. XRD (Shimata XD-D1, Japan) was used for crystal phase identification and estimation of the anastase-to-rutile ratio which were obtained at room temperature. EDX was used to measure the elemental analysis of the CNT/TiO_2 composites.

TABLE-1
NOMENCLATURES OF CNT/TiO_2 COMPOSITE SAMPLES

Samples	Nomenclatures
0.2 g MWCNT + Titanium (IV) *n*-butoxide (TNB) + benzene	CTNBB
0.2 g MWCNT + Titanium (IV) isopropoxide (TIP) + benzene	CTIPB
0.2 g MWCNT + Titanium (IV) propoxide (TPP) + benzene	CTPPB

Degradation of piggery waste: For effluent characterization, we treated aqueous piggery urine effluent, having chemical oxygen demand level approaching 50,000 mg/L, from a piggery farm in HongSeong-gun, Chungnam-do, Korea. Fig. 1 showed the procedure for characterization the piggery waste. Firstly, activated carbon (powder type) was put into as-received piggery waste and stirred for 0.5 h to absorb impurities. Then the solidification (polymer) and precipitation $[Al_2(SO_4)_3]$ were added in turn under stirring continually. A few time later, the mixture would be divided into two parts, the solid was precipitated in the bottom from the solution. We took out the solution and filtrated the solution by using activated carbon (granular type). After the filtration, the solution was treated by air blowing for 96 h and the chemical oxygen demand level could be dropped to about 535 mg/L though a physico-chemical primary treatment step (coagulation)[18,19]. The solution having chemical oxygen demand level 535 mg/L was treated by prepared CNT/TiO_2 composites by photocatalytic degradation. 0.5 g prepared composites was put into 50 mL pre-treated piggery waste having chemical oxygen demand level 535 mg/L. After irradiation of UV light for 5 h, 2 mL solution was imbibed into a standard chemical oxygen demand cell and mixed vigorously. Then the cell was thermoreacted at 148 ºC for 2 h by using a thermoreactor. After cooling to room temperature, the cell was shaken for 10 min and allowed to cool to room temperature. The chemical oxygen demand value was analyzed by a digital chemical oxygen demand meter (PhotoLab S6, WTW, Germany) in accordance with standard cell teat methods (Merck, Germany). The functional group exited in piggery waste was examined by a KBr method using FT-IR spectroscopy. Discs for the method were prepared by first mixing 1 mg of powdered oxidized multi-walled carbon nanotube with 600 mg of KBr (for FT-IR spectroscopy) in an agitate mortar and then pressing the resulting mixture successively under a pressure of 450 Pa for 3 min. The spectra of the samples were measured between 3000 and 500 cm^{-1}. The absorbance for piggery waste aqueous solution before and after degraded by CNT/TiO_2 composites under UV light irradiation were recorded by using a UV-VIS (Optizen POP, Mecasys, Korea) spectrophotometer. Total organic carbon analyzer (TOC-V CPH) was used to determine the organic compounds existed in piggery waste.

RESULTS AND DISCUSSION

Characteriztion of the CNT/TiO_2 composites: Table-2 shows the BET surface area of the CNT/TiO_2 composites. The BET surface area of CTNBB, CTIPB and CTPPB are 17.52, 27.58 and 26.64 m^2/g, respectively. It is noted that the surface area of the composite catalysts is much lower than that of neat

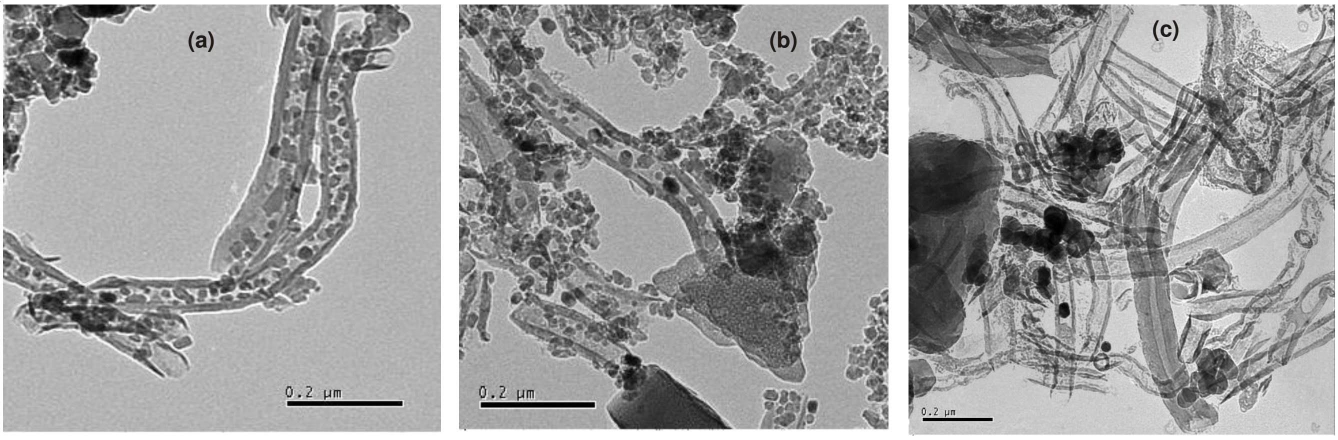


Fig. 2. TEM images of the MWCNT/TiO$_2$ composites; (a) CTNBB, (b) CTIPB and (c) CTPPB

TiO$_2$ (123 m^2/g) and multi-walled carbon nanotubes (299 m^2/g). It seems that the amount of Ti content is much more than the amount of C content in all of the composite catalysts and TiO$_2$ embedded into multi-walled carbon nanotube particles with the TiO$_2$ particles agglomerated together, thus the surface area of composites was further decreased. This result is also supported by EDX data and TEM observations.

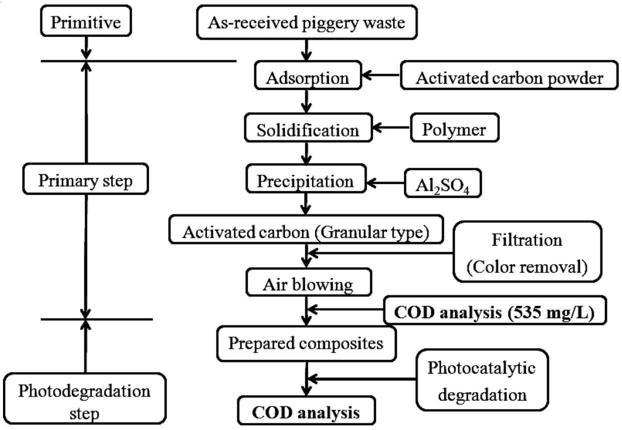


Fig. 1. Procedure for characterizing piggery waste

TABLE-2
BET SURFACE AREA OF THE CNT/TiO$_2$ COMPOSITES

Samples	S$_{BET}$ (m^2/g)
CTNBB	17.52
CTIPB	27.58
CTPPB	26.64

The morphology of the CNT/TiO$_2$ composites prepared with the multi-walled carbon nanotubes and different titanium alkoxide precursors were examined by TEM. Fig. 2 showed the TEM images of the MWCNT/TiO$_2$ composites. It was cleanly seen that TiO$_2$ particles were coated on the surface of multi-walled carbon nanotubes and the multi-walled carbon nanotube particles were dispersed homogenous with apparent agglomeration of the TiO$_2$ particles. Sol-gel method usually leads to a heterogeneous, non-uniform coating of multi-walled carbon nanotubes by TiO$_2$, showing bare multi-walled carbon nanotubes and random aggregation of TiO$_2$ onto the carbon nanotubes surface[20-22]. This result was agreement with present work. However, it was interesting to note that some of TiO$_2$ particles were embedded into the tube of multi-walled carbon nanotubes in this present work. Accordingly, a high photocatalytic yield would be expected for this special structure.

The XRD patterns of CNT/TiO$_2$ composites were shown in Fig. 3. As we know[23,24], the crystal structure of the titanium dioxide is mainly determined by the heat treatment temperature and the peaks at 25.3, 37.8, 48.0 and 62.5 are the diffractions of (101), (004), (200) and (204) planes of anatase, the peaks at 27.4, 36.1, 41.2 and 54.3 belong to the diffraction peaks of (110), (101), (111) and (211) of rutile. In our case, all of the composites were heat-treated at 973 K for 1 h. The sample CTIPB had peaks at 25.3, 37.8, 48.0, 53.8, 54.9 and 62.5 are the diffractions of (101), (004), (200), (105), (211) and (204) planes of anatase without any other peaks, indicating the CTIPB only existed in an anatase state with very strong intensity. However, the samples CTNBB and CTPPB not only had peaks at 25.3, 37.8, 48.0, 53.8, 54.9 and 62.5 are the diffractions of (101), (004), (200), (105), (211) and (204) planes of anatase, but also had peaks at 27.4, 36.1, 41.2 and 54.3 belong to the diffraction peaks of (110), (101), (111) and (211) of rutile, indicating the CTNBB and CTPPB included a mixture structure of anatase and rutile. We also observed that the sample CTNBB had stronger intensity of anatase and relatively weaker intensity of rutile, but the sample CTPPB had stronger intensity of rutile and relatively weaker intensity of anatase. Because the three kinds of titanium sources had different structures, when it was heat treated at 973 K for 1 h, these titanium sources would form to TiO$_2$ with different crystal structures. On the other hand, the characteristic peaks of multi-walled carbon nanotube could hardly be identified from the XRD patterns of CNT/TiO$_2$ composites. It was thought that the small amount of C content in the composites and the absence of multi-walled carbon nanotube aggregated pores were supported by the disappearance of multi-walled carbon nanotube characteristic peaks in XRD patterns.

The EDX spectra of CNT/TiO$_2$ composites prepared with multi-walled carbon nanotube and different titanium alkoxide precursors were shown in Fig. 4. From the spectra, all of the CNT/TiO$_2$ composites showed the peak of O and Ti, though some impure elements such as Fe, Zn, Cu, Au and V existed (which may be introduced from experimental procedure) in the samples CTNBB and CTIPB. So it could be attested that the CNT/TiO$_2$ composites were formed. The EDX elemental microanalysis (wt. %) of CNT/TiO_2 composites is listed in Table-3. From the data, we could also see that all of the samples had three kinds of major elements: C, T and O. All of the samples were rich in O and Ti elements but relatively poor in C element. This can explain the appearance of their SEM observations as mentioned above.

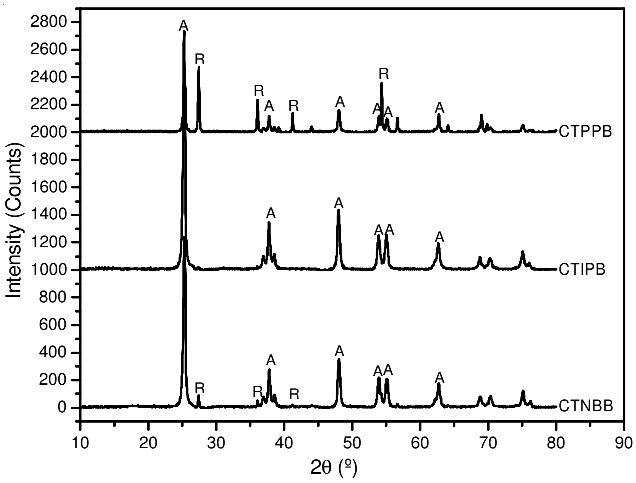


Fig. 3. XRD patterns of the CNT/TiO_2 composites

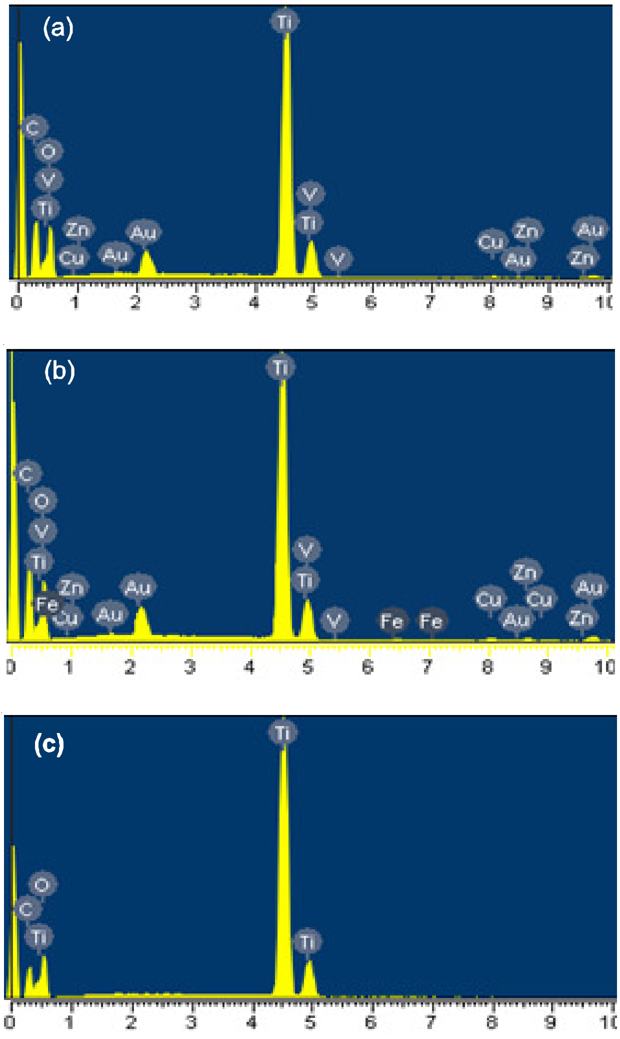


Fig. 4. EDX microanalyses of the MWCNT/TiO_2 composites, (a) CTNBB, (b) CTIPB and (c) CTPPB

TABLE-3
EDX ELEMENTAL MICROANALYSIS (wt. %)
OF CNT/TiO_2 COMPOSITES

Samples	Elements			
	C	O	Ti	Others
CTNBB	19.66	37.17	40.32	2.85
CTIPB	11.46	31.09	53.87	3.57
CTPPB	12.28	38.20	49.52	-

Degradation of piggery waste: Fig. 5 showed the chemical oxygen demand removal effect of piggery waste by degradation of CNT/TiO_2 composites prepared from different titanium precursors in benzene solvent under UV irradiation for 5 h. A significant chemical oxygen demand removal performance was also achieved by the photodegradation for all of prepared samples. After irradiation of UV light for 5 h, the chemical oxygen demand value was reduced 48, 53 and 56 % for samples CTNBB, CTIPB and CTPPB, respectively. Comparison to our previous works[18,19], the chemical oxygen demand value was only reduced about 20 % after a 2 h operating time for Ag-ACF composites and reduced about 50 % after air blowing for 72 h with K-ACF composites. It could be indicated that the prepared CNT/TiO_2 composites had excellent chemical oxygen demand removal effect.

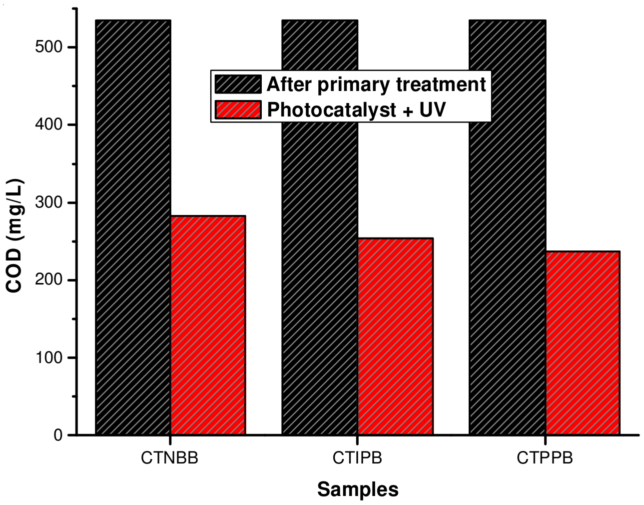


Fig. 5. COD removal efficiencies of piggery waste degradation of CNT/TiO_2 composites under UV light irradiation for 5 h

Fig. 6 showed the FT-IR result of piggery waste after primary treatment and after degradation by photocatalytic reaction on CNT/TiO_2 composites under UV irradiation for 5 h. It could be observed that important absorption bands at 800-600 cm^{-1} (attributed to C-Cl stretching), 1083 cm^{-1} (attributed C-O stretching), 1403 cm^{-1} (attributed to -C-H stretching), 1666 cm^{-1} (attributed to C=C stretching), 2087 cm^{-1} to 3050 cm^{-1} (attributed to O-H stretching) and 3120 cm^{-1} (attributed C-H stretching). These results indicated the piggery waste after primary treatment even contained various functional groups. In other words, various organic compounds exited in piggery waste after primary treatment. After degradation by photocatalytic reaction on CNT/TiO_2 composites under UV irradiation for 5 h, the important absorption bands at 694 cm^{-1} (attributed to = C-H stretching), 1045 cm^{-1} (attributed

C-O stretching), about 1565 cm^{-1} (attributed C=C stretching) and 2672 cm^{-1} (attributed O-H stretching) could be observed. Comparison with the FT-IR results of piggery waste after primary treatment, some functional groups was disappeared after degradation by photocatalytic reaction on CNT/TiO$_2$ composites under UV irradiation for 5 h.

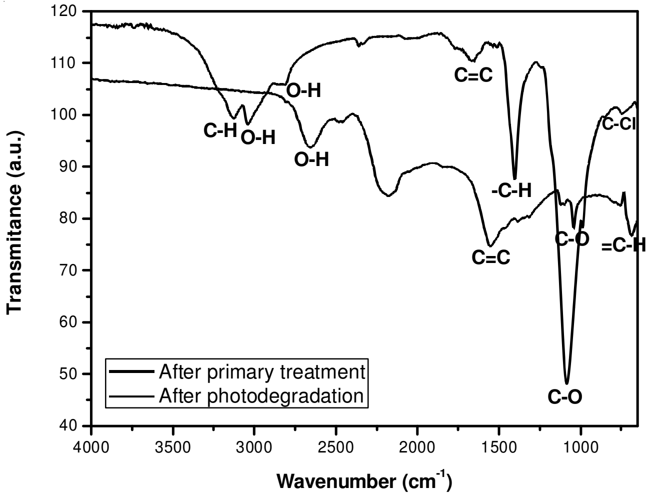


Fig. 6. FT-IR spectra of piggery waste after primary treatment and photodegradation

The removal effect of piggery waste by photocatalytic reaction on CNT/TiO$_2$ composites under UV irradiation could be also indicated by the changes of absorbance and total organic carbon of piggery waste. Fig. 7 showed the changes of absorbance and total organic carbon values of piggery waste after primary treatment and after degradation by photocatalytic reaction on CNT/TiO$_2$ composites under UV irradiation for 5 h. It was clearly observed that the absorbance of piggery waste after degradation by photocatalytic reaction on CNT/TiO$_2$ composites under UV irradiation for 5 h was much lower than that of piggery waste after primary treatment, indicated the concentration of piggery waste was decreased after UV irradiation for 5 h containing CNT/TiO$_2$ composites. The total organic carbon of piggery waste after primary treatment was 632 mg/L. After degradation by photocatalytic reaction on CNT/TiO$_2$ composites under UV irradiation for 5 h, the total organic carbon of piggery waste was reduced to 348 mg/L. It was indicated that the CNT/TiO$_2$ composites had degradation rate of 40 %. It could be also indicated that the organic compounds in piggery waste was degraded to other matters.

According to the FT-IR results, it is suggested that the piggery waste after primary treatment contained C-Cl, C-O, -C-H, C=C, O-H and C-H organic groups with big molecule. So it is assumed that one of aliphatic compounds containing these organic groups which might exit in piggery waste, as $Cl_3CC_6H_4COOH$. Most organic molecules undergo photocatalytic degradation when irradiation in the presence of a photocatalyst. This occurs through a multistep process involving the attack of the substrate by radical species, among which the OH$^•$ radical was recognized to be the most powerful oxidant[25,26]. The possible reactions were shown below: after adsorption of the aliphatic compound to the surface of TiO$_2$, the aliphatic compound was transferred to three parts CH_3COOH,

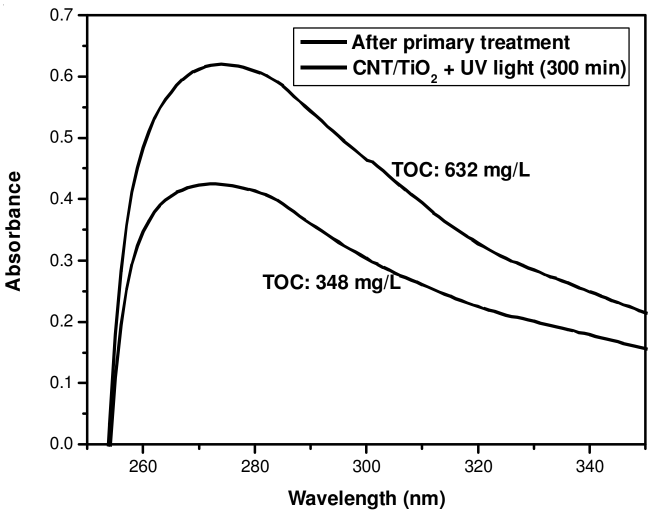
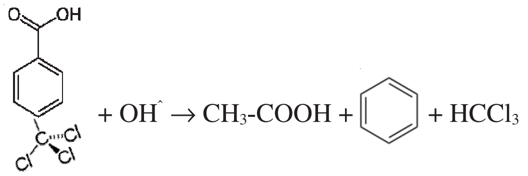


Fig. 7. Changes of absorbance of piggery waste after primary treatment and piggery waste after degradation by photocatalytic reaction on CNT/TiO$_2$ composites under UV irradiation for 5 h

C_6H_6 and $HCCl_3$ by attack of OH$^•$ (eqn. 1). The CH_3COOH was transferred to HCCOOH or HCOOH by attack of OH$^•$ (eqn. 2) and mineralized to CO_2 and H_2O by further photodegradation (eqn. 3). The $HCCl_3$ was transferred to inorganic ions by irradation of light (eqn. 4). For C_6H_6, the two initial photooxidations were enhanced by preferential attack of OH$^•$ radicals at the carbon atoms (eqn. 5) and direct oxidation of C_6H_6 was by photooxidation caused by holes in TiO$_2$ (eqns. 6 and 7). These reactions led to the generation of CHO-CH=CH-CH=CH-CHO (eqn. 8). The intermediates CH_3-CHO and $HOCH_2$-CH=CH-CHO were generated from scission of the C=C fragment (eqn. 9). The carbon atoms of the $HOCH_2$-CH=CH-CHO intermediate were photodecomposed to CHCOOH and HCHO, *via* CH_3-CHO and CH_3COOH (eqn. 10). The final products were CO_2 and H_2O by further photodegradation (eqn. 3).

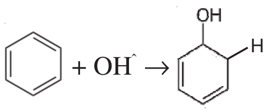


(1)

$$CH_3\text{-}COOH + OH^{\bullet} \rightarrow HCCOOH + H_2O \text{ or } HCOOH + H_2O + CO_2 \quad (2)$$

$$HCCOOH \text{ or } HCOOH + OH^{\bullet} \rightarrow H_2O + CO_2 \quad (3)$$

$$HCCl_3 + h\nu \rightarrow \text{inorganic ions} \quad (4)$$



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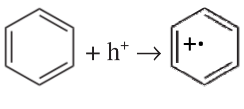

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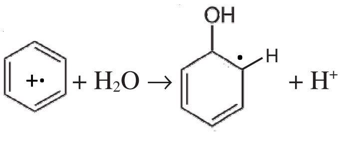

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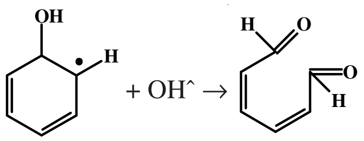

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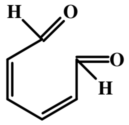

$$+ \mathrm{OH}^{\wedge} \rightarrow \mathrm{CH_3\text{-}CHO} + \mathrm{HOCH_2\text{-}CH{=}CH\text{-}CHO} \quad (9)$$

$$\mathrm{HOCH_2\text{-}CH{=}CH\text{-}CHO} + \mathrm{OH}^{\wedge} \rightarrow$$
$$\mathrm{CHCOOH} + \mathrm{HCHO} + \mathrm{H_2O} + \mathrm{CO_2} \quad (10)$$

Conclusion

In this study, we present the synthesis, characterization of CNT/TiO_2 composites. Very small BET surface area was obtained in present case for all of the composites. The TEM images showed the multi-walled carbon nanotube particles were dispersed homogenous with apparent agglomeration of the TiO_2 particles. The XRD patterns vary with strong peaks of the anatase in sample CTIPB and with a mixture of anatase and rutile in samples CTNBB and CTPPB. The EDX spectra showed the three kinds of major elements of C, Ti and O with a small amount of impure elements. Finally, we used the prepared CNT/TiO_2 composites to decompose the piggery waste under UV irradiation. The decomposition effect was analyzed by using the chemical oxygen demand method, FT-IR spectra, absorbance and total organic carbon. According to the results, after UV irradiation for 5 h, it seemed all of the samples have an excellent removal effect of chemical oxygen demand. The chemical oxygen demand value was decreased 50 % and the organic compounds in piggery waste were degraded to other matters.

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