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Research article

# Carbon nitride/titania nanotubes composite for photocatalytic degradation of organics in water and sludge: Pre-treatment of sludge, anaerobic digestion and biogas production

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ABSTRACT

In this study, carbon nitride/titania nanotubes ($C_3N_4/TiO_2$ NTs) composites were synthesized for the enhanced visible light mediated photocatalytic degradation and pre-treatment of wastewater sludge for enhanced biogas production. The co-existence of $C_3N_4$ and TiO2 NTs and visible light activity was confirmed by XRD, TEM, UV–visible and PL spectroscopy. The photocatalytic performance of $TiO_2$ NTs with 2% of melamine (precursor of $C_3N_4$), enhanced the degradation of 2-chlorophenol (2-CP) ($k = 0.0176\ min^{-1}$), where 96.6% removal was achieved at optimum pH 7.0 and 2-CP concentration of 30 mg/L. On the other hand, the application of $C_3N_4/TiO_2$ NTs for solubilization of the rigid structure of sludge by photocatalysis released the soluble organics showing an improvement in sCOD production (4587 mg/L). Subsequently, anaerobic digestion of solubilized sludge has improved the methane production (723.4 ml $kg^{-1}$ VS) by 1.37 and 1.6 times compared to that in anaerobic digestion with photolytic and raw sludge, thus showing a promising applicability for biogas production from sludge and wastewater treatment.

## 1. Introduction

$TiO_2$ materials have been widely applied in various applications in the form of various morphologies, such as zero-dimensional nanoparticles, one-dimensional nanotubes, two-dimensional sheets or layers, and three-dimensional sphere-like structures (spheres) (Fattakhova-Rohlfing et al., 2014). $TiO_2$ nanotubes (NTs), in particular, one dimension material has gained momentous scientific interest because of their unusual physical properties with a well-regulated nanotubular structure (Wang and Huang, 2016). In specific, their electronic properties, including quantum confinement effects or a high electron mobility, high surface to volume ratio, low dimensionality, are of great interest. As a consequence, the activity of $TiO_2$ NTs significantly enhanced (Mazierski et al., 2017). Considering their unique properties, these structures can be applied as an efficient photocatalyst; however, its activity is restricted to the high energy ultraviolet light with wavelength of > 387 nm i.e. only 3–5% of solar light fraction and large band of 3.2 eV (Li et al., 2016; Sun et al., 2017).

To overcome this limitation, combining $TiO_2$ with a material of narrow band gap and having suitable band gap position to form a heterojunction is an effective approach to improve light absorption, improve charge separation and electron transport, thus improving overall photoelectrochemical activity (Su et al., 2016; Anjum et al., 2016a). Previously, several studies were executed to synthesize visible-light photocatalysts by coupling $TiO_2$ with noble metals (Yoo et al., 2013), doping with ions (Yuan et al., 2013), composites with non-metal compounds (Li et al., 2016), sensitization by organic dyes or inorganic complexes (Mba et al., 2013), co-doping (Jaiswal et al., 2012), and doping with rare earth elements (Mazierski et al., 2017). However, these modifications may induce serious environmental and health and environmental problems due to the use of toxic metals, thus limiting their broad applications (Su et al., 2016).

During the recent year carbon nitride ($C_3N_4$) has been developed as a stable and visible light responsive catalyst. To date, it has been reported to display excellent photocatalytic activity and used in various applications such as in $H_2$ production, sterilization, oxidation of organics, oxygen reduction reactions and pollutant degradation (Li et al., 2016; Su et al., 2016). $C_3N_4$ is becoming a promising candidate due to its narrow band gap energy (2.7 eV) (Zhang et al., 2016). It is only composed of earth-abundant elements carbon and nitrogen, which are non-toxic and inexpensive. Moreover, it has a superior photocorrosion resistance because of the strong bonds between carbon and nitride (Su

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**Acronyms**

| | |
|---|---|
| AD | Anaerobic Digestion |
| XRD | X-ray Diffraction |
| PLS | Photoluminescence Spectroscopy |
| TEM | Transmission Electron Microscopy |
| 2-CP | 2-Chlorophenol |
| OMRE | Organic Matter Removal Efficiency |
| VS | Volatile Solids |
| TC | Total Carbon |
| sCOD | Soluble Chemical Oxygen Demand |
| tCOD | Total Chemical Oxygen Demand |
| UV | Ultra Violet |

et al., 2016).

Considering the unique properties of $C_3N_4$, heterogeneous composite of $TiO_2$ NTs with $C_3N_4$ is likely to present promising photoelectrochemical performance. It has been proposed that the $TiO_2$ (UV light active) can be combined with the $C_3N_4$ (visible light active), and the built-in electric field at the interface of $C_3N_4$ and $TiO_2$ can prevent the recombination of the photogenerated electrons and holes (Su et al., 2016). When combining $C_3N_4$ with $TiO_2$ NTs, the electrons generated from the conduction band of $C_3N_4$ will inject into CB of $TiO_2$ material, thereafter transport along long axis of NTs for reduction reaction, in the meantime holes from a valence band of $TiO_2$ will migrate to VB of $C_3N_4$ for the oxidation reaction, thus resulting an effective charge separation and transfer capability (Su et al., 2016).

The present study aims to develop a heterojunction $C_3N_4/TiO_2$ NTs and evaluate multifarious environmental applications using visible light photocatalysis process. The degradation of organic pollutants in wastewater and solubilization of wastewater activated sludge for enhancing anaerobic biogas production has been considered as a potential application for the current nanocatalyst composite.

## 2. Material and methods

### 2.1. Chemicals

Chemicals used for the synthesis of the catalyst were $TiO_2$ powder (P-25 Degussa Co.) and Melamine ($C_3H_6N_6$, Sigma Aldrich). The 2-CP (Merck) was used for the preparation of synthetic solutions of various pollutant concentrations by dissolving the suitable amount in deionized water. The culture media were prepared using chemicals (Sigma Aldrich) required for media recipe no. 195 (DSMZ, 2015). For COD analysis LCK514 COD kits were used.

### 2.2. Synthesis and characterization of the photocatalyst

$TiO_2$, P-25 Degussa, has been used as a precursor of $TiO_2$ NTs, while $C_3H_6N_6$ was used for $C_3N_4$. The composite was fabricated using high-temperature calculation method in two steps. First, the $TiO_2$ NTs were prepared by hydrothermal method (Lee et al., 2011) using $TiO_2$ powder. In the second step, a measured amount (1, 2 and 4 wt % of $TiO_2$ NTs) of $C_3H_6N_6$ was added in 2 ml of deionized water separately in crucibles and heated at the hot plate at 60 °C to get a transparent solution. Afterwards, a fixed amount (weight %) of $TiO_2$ NT was added in each solution and dried for 8 h in an oven. Finally, the mixtures were heated in a muffle furnace at 550 °C (with a heating rate of 5 °C/min) for 2.5 h. The final products formed were $C_3N_4/TiO_2$ NTs composites containing a different proportion of $C_3N_4$. For comparison, the pure $C_3N_4$ was prepared by calcination of $C_3H_6N_6$ alone at 550 °C under similar conditions as mentioned above. All synthesized materials were washed several times using deionized water and acetone and oven dried at 80 °C for 12 h.

The synthesized materials were characterized by using various instrumentations such as x-ray diffraction (XRD, PAN analytical, X'pert PRO-MPD) in the range, 10–90° 2$\theta$, using Cu K$\alpha$ radiation ($\lambda$ = 0.15405 nm), UV–visible near infrared (UV-VIS-NIR, VARIAN, Cary 5000, USA) spectrophotometry, photoluminescence spectroscopy (PLS record at Fluorescence Spectro-fluorophotometer, model RF-5301 PC, Shimadzu, Japan), and field emission transmission electron microscopy (FE-TEM, TecnaiG2 F20, FEI, USA) operating at an accelerating voltage of 200 KV.

### 2.3. Photocatalytic degradation of 2-chlorophenol

The photocatalytic activity of $C_3N_4/TiO_2$ NTs composites was evaluated in a visible light photochemical reactor (Luzchem, LZC 4V, Canada) using 2-CP solution and catalyst under continuous aeration and stirring conditions. The photocatalyst reactor was equipped with a built-in shaking system and thirteen (104W) cool white lamps (Sylvania s068) as a source of visible light. In the initial experiments, the photocatalytic activity of the prepared catalysts $TiO_2$ NTs, $C_3N_4$ and $C_3N_4/TiO_2$ NTs composites (containing a different concentration of melamine) were evaluated to find out the best suitable concentration of melamine used for the preparation of the composite. Each of the experiments was performed with a photocatalyst dose of 0.05 g dispersed in 100 ml volume of 40 mg/L of 2-CP solution in a quartz beaker place in the reactor. The degradation of 2-CP was optimized for pH and pollutant concentration by providing the solution pH ranges from (3–10) and pollutant concentrations (20–70 mg/L) in different runs. The reusability of $C_3N_4/TiO_2$ NTs was tested for 4 times cycles using the optimum experimental conditions. The photocatalytic degradation was measured by analyzing the amount of 2-CP remained in the solution after each experiment using 2.5 ml of the sample in UV–vis spectrophotometer (LANGE DR-6000, HACH, Germany) at a wavelength of 274 nm.

### 2.4. Pretreatment of wastewater sludge

The photocatalyst was also tested for its applicability using as a pretreatment of waste activate sludge)which is complex in nature and difficult to degrade(to enhance its anaerobic digestion (AD). The sludge sample was collected from a centralized industrial wastewater treatment plant of the Jeddah industrial city (21° 23′ 59″ N, 39° 13′ 40″ E), Saudi Arabia, possessing more than five hundred industries. The pretreatment of sludge was performed a cylindrical photochemical Pyrex reactor equipped with an aeration and the magnetic stirring system. A visible light lamp (150 W) is fixed in a central glass tube containing a continuous water circulation system for cooling. The glass column of the reactor contains three outlets, fixed with pH probe, aeration pipe, and substrate sampling reactor. For pretreatment, the column was filled with the fresh sludge (2% w/v) up to 1L at the catalyst ($C_3N_4/TiO_2$ NTs) dose of 0.5 g/L. The initial pH of the system was adjusted between 5.0 and 7.0 and the pretreatment process was conducted for 6 h. In another run, the pretreatment was performed without the addition of catalyst (photolysis) as a comparison test. The samples of the sludge were taken at regular intervals and solubilization efficiency was analyzed by measuring tCOD, sCOD and VS removal.

### 2.5. Anaerobic digestion of pretreated sludge

For AD experiments, methanogenic bacteria were used as a mixed culture taken from cow manure. The cow manure was collected from the Agricultural Research Station of King Abdulaziz University situated at Hada Al-Sham, Saudi Arabia. The culture media recipe no. 195