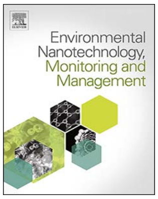
Environmental Nanotechnology, Monitoring & Management 8 (2017) 103–111

Contents lists available at ScienceDirect

Environmental Nanotechnology, Monitoring & Management

journal homepage: www.elsevier.com/locate/enmm



# Photoelectrocatalyst of Fe co-doped N-$TiO_2$/Ti nanotubes: Pesticide degradation of thiamethoxam under UV–visible lights

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## ARTICLE INFO

*Keywords:*
Fe-N- $TiO_2$/Ti
Thiamethoxam
Nanotube
Photoelectrocatalyst
Degradation

## ABSTRACT

Preparation of titanium dioxide ($TiO_2$) had been carried out by anodizing method that was continued by Nitrogen (N) and Iron (Fe) doping to obtain the Fe-N-$TiO_2$/Ti electrode through sol-gel method. The synthesis of Fe-N-$TiO_2$/Ti by adding $NH_4Cl$ as a source of N and $Fe(NO_3)_3$ as a source of Fe were prepared by dip-coating technique. The photocurrent response of $TiO_2$/Ti and Fe-N-$TiO_2$/Ti tested in photoelectrocatalyst showed the $TiO_2$/Ti electrode was active in UV light and Fe-N-$TiO_2$/Ti was active in the visible light. The XRD and SEM characterizations result of Fe-N-$TiO_2$/Ti was the forming of anatase crystal and nanotube structure. The FTIR data was indicated the presence of Fe—O and Ti—N bonds on the wavenumber of 580 $cm^{-1}$ and 509 $cm^{-1}$, respectively. The degradation result of thiamethoxam pesticide compound in photoelectrocatalyst showed the $TiO_2$/Ti electrode was active on the UV light irradiation with degradation rate constant 0.0436 $min^{-1}$ and Fe-N-$TiO_2$/Ti was active in the visible irradiation with the degradation rate constant 0.0580 $min^{-1}$.

## 1. Introduction

The development of technology in agricultural field had been opening the opportunity for the pesticide users. However, the presence of pesticide organic compound in the groundwater, surface water, the wastewater of pesticide industries, the processing of liquid wastewater and the other drinking water sources needs to be controlled because the pesticide is in Dangerous Poisonous Substance (DPS) wastewater category (Mir et al., 2013). The pollution of organic pesticide contaminated in nature can harm the living things and environment. Meanwhile, the natural biodegradation process works very slowly along with the accumulation of excess waste from industry, or the residue of organic compounds that has been used broadly as herbicide, insecticide, and the plant growth controller, that accumulate in the water. One example of synthesized pesticide is thiamethoxam that is thio-nicotinyl subclass in nicotinoid insecticide group (Zabar et al., 2012; Yang et al., 2014a). The pesticide activities can be classified as superior in controlling the pests, but it has the characteristic of being difficult to be degraded by land and it has high mobility so it has the potential of releasing into the aquatic environment as contaminants.

A method that can process the pesticide wastewater to be environmentally friendly compounds is needed. Nowadays, there has been many methods used to decrease the pesticide pollution biologically and chemically, one of them is by using the advance oxidation processes such as the usage of photocatalyst for photodegradation (Maulidiyah et al., 2015a; Nurdin et al., 2016a; Nurdin et al., 2016b). The photodegradation has been developed in this last decade based on the photoelectrocatalyst using $TiO_2$ semiconductor (Nurdin, 2014; Maulidiyah et al., 2015d; Maulidiyah et al., 2015e). Photoelectrocatalyst is a method of combining the electrochemistry process and the photocatalyst process to raise the photocatalyst performance (Nurdin and Maulidiyah, 2014; Arham et al., 2016). This method has several advantages in chemical sensor and organic pollutant can be degraded quickly to be harmless compounds such as $H_2O$ and $CO_2$, and it becomes more efficient in using the chemical substances and the energy (Maulidiyah et al., 2015b; Maulidiyah et al., 2015c; Dali et al., 2016).

The optimation of $TiO_2$ usage by using the sunlight to earth approximately 3–5% and the low efficiency of the result ($< 10\%$) caused electrons recombination was too quickly between the electron and the hole (Nurdin et al., 2009). The way to solve it was minimizing the energy gap by doping either the metal or non-metallic atoms. The doping of non-metal such as C (Maulidiyah et al., 2015f), S (Tang and Li, 2008), P (Zhang et al., 2009), N (Maulidiyah et al., 2015a) and B (Bessegato et al., 2014) were proven to be effective in shifting the optical absorption of $TiO_2$ to the lowest level of energy. From the various non-metallic elements, N is the most effective dopant because its size is not quite different from oxygen and its low ionization energy. Besides, N also improves the optical characteristic of $TiO_2$ so that it can increase the quality of the thin layer (Kalantari et al., 2016).

Beside the non-metal, immobilization of transition metal Cr (Yang

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http://dx.doi.org/10.1016/j.enmm.2017.06.002
Received 25 February 2017; Received in revised form 16 May 2017; Accepted 8 June 2017
2215-1532/

et al., 2014b), Cu (Liu et al., 2015), Fe (Tang et al., 2014), Ni (Lin and Shih, 2016) and Ag (Nurdin et al., 2016c) were also successful to activate $TiO_2$ on the visible light and increase the performance of the photoelectrocatalyst cells. Among the transition metals, Fe was good to be used because its ionic radius was almost the same with that of $Ti^{4+}$ so that $Fe^{3+}$ ions would probably be easier to substitute $Ti^{4+}$ ions in the crystal lattice of $TiO_2$. The doping method was one of the $TiO_2$ modifications that changed the electronic structure of $TiO_2$ so that it decreases the band gap energy. The study by Dolat et al. showed that the $TiO_2$ modification by choosing the suitable Fe and N could produce high photocatalytic activities under the visible light (Dolat et al., 2013).

In this research, the fabrication of double doped Fe-N-$TiO_2$/Ti working electrode, that has a role to degrade the pesticide test compound (thiamethoxam) in observing the efficiency level to degrade the thiametoxam in the water, was done.

## 2. Experimental section

### 2.1. Preparation of Ti (titanium) plate

The preparation of Ti (titanium) plate was done by cutting the Ti plate with the purity of 99%, the thickness of 0.5 mm and the size of 4 cm × 0.5 cm then it was sanded by using 1200CC soft sand paper until the surface was clean and shiny. It was then washed by using the detergent solution, water, and distilled water. After being dried in the air, the Ti plate was submerged (etching) in the mixture solution of HF, $HNO_3$, and destilled water with the ratio of 1:3:6 for 2 min. The last stage was rinsed the Ti plate with destilled water to remove the remaining etching solution on the surface of Ti plate and drying it in the air.

### 2.2. Preparation of $TiO_2$ layer by anodizing method

The titanium plate was prepared by putting into a probe and added the electrolyte solution of 0.27 M NH4F and distilled water in 98% glycerol. The anodizing process was performed by putting the Ti plate as an anode and Cu plate as cathode using magnetic stirrer, and giving the potential bias of 25 V that was connected to the power supply. This anodizing process was done in 4 h and calcined the Ti plate for 1.5 h at the temperature of 500 °C.

### 2.3. $TiO_2$/Ti doping process with iron (Fe) and nitrogen (N) by using sol-Gel method

$TiO_2$ doped Fe and N were prepared by two solutions. The first solution was formed $TiO_2$ colloid solution which prepared by controlling hydrolysis from titanium tetra-isopropoxide (TTIP), 4 mL of it was taken in 0.5 mL acetylacetonate and 15 mL of ethanol. The second solution was 15 mL of 99% ethanol and 2 mL distilled water with the addition of 1 mL of 0.1 M acetic acid. The mixture of the first and the second solutions was refluxed for 3 h in the temperature of 50 °C. Then, it was stirred by using a magnetic stirrer for 3 h at the temperature of 50 °C that was followed by the addition of $NH_4Cl$ and $Fe(NO_3)_3$ to produce the $TiO_2$ sol containing Fe and N. The sol produced was evaporated at the room temperature for 48 h until it formed gel. After that, the gel produced was heated in an oven at the temperature of 80 °C for 30 min. The coating process was done by dyeing process on the area overgrown by $TiO_2$ on the titanium plate. The dyeing process was done for 10 min and it was lifted slowly. Then, it was calcinated in an oven for 15 min at the temperature of 150 °C.

### 2.4. Degradation of thiamethoxam pesticide by photoelectrocatalysis system

#### 2.4.1. Determination of thiamethoxam pesticide standard curve

The determination of thiamethoxam standard curve was done by using the thiamethoxam solution with the concentration of 0.7, 1.4, 2.1 and 2.8 ppm and it was dissolved with 0.1 M of $NaNO_3$. Then, the absorbance value from each thiamethoxam concentration were determined by using UV–vis spectrophotometer. The standard curve was made by plotting the thiamethoxam concentration versus the absorbance value.

#### 2.4.2. Degradation test of thiamethoxam pesticide

The thiamethoxam degradation test of 0.7, 1.4, 2.1 and 2.8 ppm (+0.1 M $NaNO_3$) was done by Multi Pulse Amperometry (MPA) method for 10 min and the potential difference of 0.5 V with the variation of UV and visible lights. Every 10 min in an hour the absorbance measurement was done by using UV–vis spectrophotometer to know the concentration decreasing of thiamethoxam pesticide.

## 3. Results and discussion

### 3.1. Synthesis of $TiO_2$/Ti and Fe-N-$TiO_2$/Ti electrodes

The preparation of $TiO_2$/Ti nanotube by direct oxidation electrochemical was done by using copper (Cu) as cathode for 4 h with the potential bias of 25.0 V. The solution of $NH_4F$ and glycerol as electrolyte on the anodizing process was used to decrease the current fluctuations and produce the softer electrode wall.

The next step was the sintering process to evaporate the organic solvents trapped in the titanium plate and to grow crystals on $TiO_2$ plate. The sintering process done in the temperature of 500 °C for 1.5 h would produce an anatase crystal structure that had better photocatalysis activities than the other kind of crystals because the anatase $TiO_2$ was more photoactive than the rutile as the surface area of anatase was larger than the rutile so the active side per unit of anatase was bigger than that of rutile (Nurdin et al., 2017a; Nurdin et al., 2017b). The structure of anatase had 3.2 eV band gap that was similar with the UV light wave energy with the wavelength of ($\lambda < 380$ nm) (Gupta and Tripathi, 2011). This technique produced $TiO_2$/Ti formed on the surface of Ti plate, appeared visually that the $TiO_2$ layer gained from the anodizing method was quite homogenous and the thickness of the layer was quite good (Fig. 1a).

The Fig. 1b showed the sol-gel filled the matrix or the distribution media of ionic dopant, acetyl acetonate had a role as chelating ligands that would produce exothermic reaction and turned the solution to be yellow. Whereas for doping the Fe and N, Fe $(NO_3)_3$ as the source of Fe and ($NH_4Cl$) as the source of N were added to the formed sol, visually it seemed that the $TiO_2$/Ti electrode was coated by the sol-gel.

### 3.2. Characterization of working electrodes

#### 3.2.1. X-ray diffraction (XRD) characterization

The measurement by X-Ray Diffraction (XRD) was aimed to get the information on the crystal structure of $TiO_2$/Ti working electrodes and Fe-N-$TiO_2$/Ti. The different absorption peaks among the crystals of Ti, $TiO_2$/Ti, and the Fe-N-$TiO_2$/Ti plate was shown in Fig. 2.

Based on Fig. 2 can be seen that diffractogram peak on $2\theta = 25°$ and 48° indicated the $TiO_2$/Ti working electrode formed is anatase crystal after heating at a temperature of 500 °C. According to Nurdin et al. that the rutile $TiO_2$ crystal would begin to appear when the calcination was done at the temperature of 600 °C (Nurdin et al., 2016a). The presence of diffractogram on $2\theta = 32°$, it was predicted that the absorption peak of Fe metal (Niu et al., 2014). On the other hand, the radius of $Ti^{4+}$ (0.68 A°) and $Fe^{3+}$ (0.64 A°) were almost similar, therefore, the $Fe^{3+}$ ions could involve into the titanium crystal and stayed in the lattice of $TiO_2$ crystal (Yu et al., 2009).

#### 3.2.2. Fourier transform infra red (FTIR) characterization

The FTIR analysis was done in order to strengthen the information about successful doping of Fe and N on the surface $TiO_2$/Ti. The IR spectrum of $TiO_2$/Ti and Fe-N-$TiO_2$/Ti could be seen in Fig. 3.