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Enhanced Electrochemical Degradation of 4-Nitrophenol Molecules using novel Ti/TiO₂-NiO Electrodes

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ABSTRACT

Removal of 4-Nitrophenol (4-NP) compounds by the electrochemical degradation method using Ti/TiO₂-NiO electrodes was successfully conducted. This study aims to study the activity of Ti/TiO₂-NiO electrodes in the electrocatalytic degradation of 4-NP as organic compound pollutants. Ti/TiO₂-NiO preparation was carried out by the wet impregnation technique, then TiO₂-NiO composites were sprayed on the surface of Titanium electrodes. The electrode was characterized by X-Ray Diffraction (XRD), a Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM), and Cyclic Voltammetry (CV). A Diffractogram XRD of TiO₂-NiO composites showed a characteristic peak of TiO₂-NiO at 2θ =33°. Meanwhile, analysis of the SEM surface morphology showed that NiO with an average particle size of 22.07 µm can be attached to the surface of the Ti/TiO₂ plate. Electocatalytic degradation of 4-NP compounds was found to be optimum at pH 11 and 80 minutes electrolysis time with a rate constant of 0.0373 min⁻¹. The electrochemical degradation exhibited the percentage of removing 4-NP rate of more than 95% with good electrode measurement stability.

Keywords: Nanotechnology; water purification; degradation; 4-Nitrophenol; Ti/TiO₂-NiO

INTRODUCTION

Global warming and the fast pace of industrial development is a significant factor in triggering environmental pollution, especially pollution in sources of clean water. 4nitrophenol (4-NP) is a phenolic compound that has a nitro group and is quite widely used in various industries such as petrochemical manufacturing, leather tanning (dark leather), rubber (chemical rubber), wood preservation, fungicides and pharmaceuticals [1-3]. However, the wide use of 4-NP compounds is concerning due to their good solubility level in the water, high level of toxicity, and the fact that they are not easily degraded by the environment [4]. Short term exposure to 4-NP may harm human's health as it leads to respiratory problems, headaches, and cyanosis, while long-term exposure to 4-NP can cause gene mutations in organisms and injury to blood cells [5]. Therefore, degradation of the contamination of 4-NP compounds in water is a topical and crucial issue to study. Several previous studies have revealed ways to eliminate the content of 4-NP in water by means of adsorption [6, 7], denitrification [8], ozonation [9, 10], photodegradation [1, 11] and electrodegradation [12, 13].

However, currently, there are only a few types of research on the use of electrodegradation to remove 4-NP from the water. This underlines that this topic is underdeveloped despite the fact that the degradation of a compound electrochemically is known to offer many benefits since it is easy to operate, affordable, environmentally friendly and more effective [14]. Also, the addition of electrical potential to the electrodegradation system can increase the electron transfer rate and electric current to increase the activation of the material used as an electrode and the degradation process of organic compounds [15]. In this study, TiO₂-NiO-based electrode composites will be

developed to coat Ti electrodes since the electrode is an important component in the process of electrochemical degradation.

At present, the most commonly used electrodes for degradation are Pt, carbon, and graphite electrodes [16-18]. However, these electrodes are not highly recommended since they are expensive, have unstable prices, and are easy-to-fall which may impede an optimum degradation process. In fact, several studies have reported that the making of electrodes by combining several semiconductor materials provides sufficient results such as Ti/RuO₂-Pt [19], Ti-IrO₂-Pt [20], RuO₂-PdO-TiO₂/Ti [21], and Ti/SnO₂-Sb₂O₅-IrO₂ [22]. Previous research has reported that TiO₂ is able to degrade and eliminate organic compounds and produce final products in the form of CO₂, SO₄²⁻, NH₄⁻, and NO₃ [23, 24]. However, the use of TiO₂ powder to degrade organic compounds is less efficient because TiO₂ powder is easily dispersed in water, making it difficult to regenerate. This is the reason why its use for the photodegradation process is limited because the light radiation used is not able to activate all of the photocatalyst particles due to its extremely turbid mixtures. Therefore, the making of a semiconductor thin layer on an electrode substrate is considered as an innovation to obtain anode electrodes that are easy to handle because they can easily separate electrodes from degraded solutions and are easy to regenerate.

The TiO₂-NiO composite is one way to reduce the weakness of TiO₂ material which has a high energy gap (3.23eV). NiO is one of the metal oxides which has a low energy gap and good electrochemical and conductivity activity in the form of composites such as Ti/Co-NiO [25], CNT@NiO [26, 27] and graphene/NiO [28]. In this study, Ti/TiO₂-NiO electrodes have been developed for the degradation of organic compounds as pollutants in water such as 4-NP. This TiO₂-NiO composite can show good

performance in the 4-NP degradation process because it can facilitate electron transfer rates from water splitting to produce electrons for the 4-NP reduction process.

METHODOLOGY

Materials and apparatus

4-Nitrophenol was purchased from Sigma Aldrich Singapore (molecular formula $C_6H_5O_3N$ molecular weight 139.11), TiO₂ with a particle size <100 nm (Sigma Aldrich), NiNO₃.6H₂O (Sigma Aldrich), Titanium metal from Baoji Qixin Titanium Co.Ltd, poly(vinyl alcohol) (PVA) (Merck), ethanol p.a. (Merck), NaCl (Sigma Aldrich), H₂O₂ (Merck). All of the chemical reagents used were of analytical grade.

The prepared materials were characterized by X-ray diffraction (XRD) (X' Pert Pro Philips, Cu K α radiation, $\lambda = 0.154,056$ nm, $2\theta = 5$ o - 80 o), a scanning electron microscope (SEM) MERLIN with a powerful 5000x zoom, a transmission electron microscope (TEM, JEOL JEM-2100) and a potentiostats eDAQ ER466.

Synthesis of TiO2-NiO composite

1.145 grams of technical TiO₂ were added to 0.81 grams of NiNO₃.6H₂O which had been dissolved in 25 mL of distilled water. The solution was stirred for 60 minutes until reach homogeneous solution. The green mixed solution was then oven heated at 110 °C for 3 hours to increase the NiO crystals. Once the distilled water evaporated and a green suspension was formed, it was calcinated at a temperature of 700 °C with a furnace speed of 10 °C/minute.

Preparation of Ti/TiO2 and Ti/TiO2-NiO electrodes

Preparation of Ti/TiO_2 electrodes was carried out by mixing 12.5 grams of synthesized TiO_2 and 1 gram of PVA into 50 mL ethanol, then sterilized and sonicated

for 15 minutes until they were dispersed. The TiO_2 dispersion was then sprayed on a titanium plate and heated at 200 °C for 15 minutes. Meanwhile, preparation of the Ti/ TiO₂-NiO electrodes was carried out by mixing 12.5 grams of synthesized TiO₂-NiO and 1 gram of PVA into 50 mL ethanol. Then they were sterilized and sonicated for 15 minutes until dispersed. The dispersion of TiO₂-NiO was then sprayed on a titanium plate and heated at 200 °C for 15 minutes.

Degradation of 4-NP electrocatalytic study

Electrochemical degradation of the 4-NP solution resulted from a batch system at 100 mL container capacity using 2 electrodes of Ti/TiO₂-NiO as an anode and Ti electrode as a cathode (width of each electrode is \pm 1.5 cm, length is of 7 cm, and the surface area of the electrode is of 7.5 cm²). 4-NP degradation was carried out in 50 mL with an initial concentration of 10 mg/L in a supporting electrolyte solution of 500 mg/L NaCl and 10 mM H₂O₂. Various pH and electrolysis time were observed to produce optimal degradation of the 4-NP molecules. The measurement of 4-NP solution degradation was carried out using the cyclic voltammetry method in the potential range of 0 to -1000 mV with a scan rate of 50 mV/s. % 4-NP degradation was calculated using equation 1.

$$\% \text{ degradation} = \frac{i_i - i_f}{i_i} \ge 100 \%$$
(1)

Where i_i is the current before degradation, and i_f is the current after degradation. Then, the kinetic constant can be calculated as following equation 2.

$$\frac{dC}{dt} = \frac{dA}{dt} = -k. t \text{ or } ln \frac{C}{C_o} = ln \frac{A}{A_o} = -k. t$$
(2)

Where C is the concentration of 4-NP after the degradation process and C_o is the initial concentration, then k can be determined from the plot of ln (C/C_o) vs. t (the time reaction).

RESULTS AND DISCUSSION

Preparation of Ti/TiO2-NiO electrodes and their characteristics

This research used commercial Titanium metal from Baoji Qixin Titanium Co.Ltd as the electrode. The Ti metal was then thinly coated with TiO₂ powder and the TiO₂-NiO composite was synthesized by a spray technique. The diffractogram of XRD from Ti, Ti/TiO₂, TiO₂-NiO and Ti/TiO₂-NiO is shown in Figure 1. These results show that in diffractogram Ti there are characteristic peaks that appear at certain diffraction angles which are the result of the diffractogram of Ti compounds. The peaks include $2\theta = 35^{\circ}$ $(d100 = 2.5550 \text{ Å}), 2\theta = 38^{\circ} (d002 = 1.0130 \text{ Å}), 2\theta = 40^{\circ} (d101 = 2.2430 \text{ Å}), 2\theta = 53^{\circ}$ $(d102 = 1.7262 \text{ Å}), 2\theta = 62^{\circ} (d110 = 1.4753 \text{ Å}), \text{ and } 2\theta = 70^{\circ} (d103 = 1.3320 \text{ Å}) \text{ which}$ is the area of Ti metal characterization in accordance with JCPDS standard No. 44-1294. The diffractogram of Ti/TiO2 is shown that the result shows that in difractogram Ti/TiO2 there are characteristic peaks as TiO₂ anatase phase. The peaks include $2\theta = 25^{\circ}$ (d101 = 3.4967 Å, $2\theta = 37^{\circ} (d004 = 2.3679 \text{ Å})$, $2\theta = 48^{\circ} (d200 = 1.8874 \text{ Å})$, $2\theta = 54^{\circ} (d105 = 1.8874 \text{ Å})$ 1.6931 Å), and $2\theta = 62^{\circ}$ (d211 = 1.6674 Å) in accordance with JCPDS standard No. 78-2486. The shape of the diffractogram that resembles amorphous characterizes amorphous silica. Referring to the previous research [29, 30], coating TiO₂-NiO composite material on Ti metal will produce Ti/TiO₂-NiO electrode material. From the results of the practice, the peaks show the presence of TiO₂-NiO composites in area $2\theta = 35^{\circ}$ (d₁₀₀ = 2.5550 Å), $2\theta = 38^{\circ} (d_{002} = 1.0130 \text{ Å}), 2\theta = 40^{\circ} (d_{101} = 2.2430 \text{ Å}), 2\theta = 53^{\circ} (d_{102} = 1.7262 \text{ Å}), 2\theta = 53^{\circ} (d_{102} = 1.7262$ 62° (d₁₁₀ = 1.4753 Å), and $2\theta = 70^{\circ}$ (d₁₀₃ = 1.3320 Å) in accordance with JCPDS standard No. 33-0960. Compared to the result of the previous research, as mentioned earlier, the results in this study are in accordance with the literature. Some of the literature states that the phase of TiO₂ will be observed as anatase, rutile phase TiO₂ and NiTiO₃. Addition of

Ni metal oxide can increase the thermal resistance of TiO_2 to phase transformation so that it can hold the anatase structure into rutile.



Figure 1. XRD patterns of Ti, Ti/TiO₂, TiO₂-NiO, and Ti/TiO₂-NiO electrodes. a.u. refers to arbitrary unit

Figure 2 shows the results of the SEM morphological characterization of the Ti, Ti/TiO₂ and Ti/TiO₂-NiO electrodes. The surface of the Ti electrode has a homogeneous and smooth surface as shown in **Figure 2a**. This is also the same for the morphological appearance of the Ti/TiO₂ electrodes since there is no significant difference between the surface of the Ti electrode and Ti/TiO₂. However, on the Ti/TiO₂-NiO electrodes, the electrode surface was not homogeneous and smooth, and it was not evenly distributed with the addition of NiO metal oxide on the electrode surface with an average particle size of 22.07 μ m. This shows that TiO₂-NiO oxide was successfully formed and bonded well on the surface of the electrode as shown in **Figure 2c**. While TEM images are shown in **Figure 3**. The image characterization shows agglomerization of TiO₂-NiO particles. However, from the XRD pattern and TEM images reveal that the material oxide has

highly crystallinity and each grain corresponds to single crystalline. The bright and dark contrast on the surface of materials as shown in Figure 3 reveal that the materials have a large surface so that the target analyte can optimally adsorb on the surface of electrode during electrodegradation process. Moreover, some references reported that the dark and bright contrast due to difference in average atomic number and particle size of TiO_2 and NiO, respectively [31, 32]. The results of elemental analysis showed that the composition of Ti/TiO_2 -NiO material contained 10.20% Ti, 9.90% Ni, and 80% O.



Figure 2. SEM morphological characterization of (a) Ti, (b) Ti/TiO₂, and (c) Ti/TiO₂-NiO electrodes



Figure 3. TEM and surface morphological characterization of Ti/TiO₂-NiO

In addition, electrode characterization was done by measuring the electrode current response using cyclic voltammetry. Measurements were made on Ti, Ti/TiO2 and Ti/TiO2-NiO electrodes with a voltammogram in Figure 4. Based on the cyclic voltammogram, it is apparent that the peak current produced by Ti/TiO₂-NiO electrodes is greater than that of the Ti and Ti/TiO₂ electrodes. This proves that the modification of other oxides on Ti/TiO₂ electrodes as a composite can increase the electron transfer rate so that the electrons produced will be relatively more numerous and produce a greater current response. This also corresponds with previous studies revealing that the presence of Ni (II) in composite systems can increase the conductivity of electrodes. In addition, besides the doping of other oxides, the increase in current and conductivity of the electrode is also influenced by several other factors such as the active surface of TiO₂, so that the electron transfer rate will occur faster which causes greater current and conductivity. These results also correspond to the results of the measurement of the crystal size of TiO₂ material from XRD diffractogram data. The calculation of crystal size using the Scherrer equation reveals that the crystal size of TiO₂ on Ti/TiO₂ electrodes is 23.2 ± 0.3 nm, while in the Ti/TiO₂-NiO electrodes it is 16.8 ± 0.2 nm. This proves that the presence of NiO can change the crystal size structure of TiO_2 , and thus prevent TiO_2 crystals from growing normally during the crystallization process.



Figure 4. Cyclic voltammogram of Ti, Ti/TiO₂, and Ti/TiO₂-NiO in 5 mmol L-1 K₃[Fe(CN)₆]/K₄[Fe(CN)₆] solution containing 0.1 mol L⁻¹ KCl

Additionally, the surface coverage of electrode can be determined by cyclic voltammetry [33, 34] in various scan rate and calculated as following equation 3.

$$i_{p} = \frac{n(1-\alpha)n\alpha AF2\nu\Gamma}{2.718RT}$$
(3)

where n is the total of number electron involved in the electroreduction of 4-NP, T is the standard temperature (T=298 K), v is the scan rate, F is the Faraday constant (96,485 C mol⁻¹), R the gas constant (8.314 J mol⁻¹ K⁻¹), A is the geometrical area of electrode (A=0.07 cm²), α is the electron transfer coefficient, n_{α} is the number of electrons involved in the rate determining step, and Γ is surface coverage of electrode. The n_{α} and α can be determined by the linear curve between potensial reduction of 4-NP vs ln scan rate as following equation 4. **Figure 5** shows the curve of scan rate of electroreduction of 4-NP vs current response to determine the surface coverage of the Ti/TiO₂-NiO electrodes.

$$E_{pa} = \text{const.} + [0.02569 \ (1-\alpha)n_{\alpha}] \ln v \ (T = 298 \text{ K})$$
(4)



Figure 5. Plot of current response of electroreduction of 1 mM 4-NP vs scan rate and potential vs logarithm of scan rate

From these results, if a flat surface electrode is assumsed, the average surface of Ti/TiO_2 -NiO electrode is estimated approximately about 2.98 x 10⁻⁷ mol m⁻². The result presents that the Ti/TiO_2 -NiO electrodes has a higher surface accumulation for adsorption of 4-NP on the surface electrode.

Electrochemical Degradation Study of 4-NP

Optimization of pH and electrolysis time during the degradation process at a potential of 5 V has been carried out. The results showed that the degradation of 4-NP was optimum at pH 11. In acidic and slightly acidic solutions, the 4-NP molecule will undergo hydrolysis and the Ni molecules will dissolve resulting in some changes in the surface of the electro-structure which cause a low percentage of degradation. Meanwhile, at an alkaline pH, the 4-NP molecule will ionize so that the molecules are completely dissolved in the system. Hence, the high OH⁻ concentration allows it to increase the

amount of hydroxyl radicals formed leading to a more optimum degradation process. The results of the pH measurements are shown in **Figure 6**.



Figure 6. Effect of pH to degradation of 4-NP 10 mg L^{-1} in a supporting electrolyte solution of 500 mg/L NaCl and 10 mM H₂O₂ with 60 minutes electrolysis time



Figure 7. Effect of electrolysis time in degradation of 4-NP 10 mg L⁻¹ with a supporting electrolyte solution of 500 mg/L NaCl and 10 mM H₂O₂ at pH 11.0

The effect of electrolysis time on 4-NP degradation was obtained optimally in 80 minutes. The effect of the electrolysis time on 4-NP degradation is shown in **Figure 7.** From the plots, it can be seen that lengthening the electrolysis time given to the system can significantly reduce the concentration of 4-NP. This proves that the electrolysis time is

sufficient to signify the degradation of organic compounds, especially 4-NP. Ti/TiO₂-NiO electrodes show a relatively shorter time for the degradation of 4-NP compared to Ti electrodes and Ti/TiO₂ electrodes. The calculation of the kinetic rate constant shows that the Ti/TiO₂-NiO electrode has a value higher than the Ti and Ti/TiO₂ electrodes. The linear plotting between the $ln(C/C_o)$ versus the electrolysis time (t) indicates that the degradation followed the first-order kinetics mechanism. The kinetics rate constant (k) can be determined from the slopes of the linear regression. The calculation of the kinetics rate constant shows that the Ti/TiO₂ electrodes. The calculation results of the degradation rate and a comparison with several previous studies are shown in **Table 1**.

Materials*	Degradation Rate, $k (min^{-1})$	Method	Reference
Ti ed.	0.0021 + 0.0002	electrochemical	this work
Ti/TiO_2 ed.	0.0071 ± 0.0002	electrochemical	this work
Ti/TiO ₂ -NiO ed.	0.0373 ± 0.0046	electrochemical	this work
Ag@CeO	0.0054	photocatalysis	[35]
rGO-ZnS	0.0300	photocatalysis	[36]
Ag-MOF	0.1980	catalytic reaction	[37]
Bi ₂ O ₃	0.0290	photocatalysis	[11]
TiO ₂	0.0051	photocatalysis	[11]
Au-NPs-NGQDs	0,7044	photocatalysis	[38]
ZnO	0.0058	photocatalysis	[39]
$Ce-PbO_2 ed.$	0.0377	electrochemical	[40]

Table 1. The degradation rate of 4-NP using Ti, Ti/TiO₂ and Ti/TiO₂-NiO electrodes

* ed. refers to electrodes

The lengthy electrolysis time allows for high production of hydroxy radicals leading to a more optimal degradation process. When referring to measurements using a cyclic voltammogram (CV), it is noticeable that the 4-NP structure experiences some changes before and after the degradation process. The mechanism for the breakdown of the 4-NP

compound is shown in **Figure 7**. The degradation of 4-NP in this study may be done through various methods, one of which is a reduction of the nitro group to primary amine and degradation by hydroxy radicals resulting from the breakdown of H_2O_2 compounds in cathode. The 4-NP breakdown that becomes a 4-nitrocatechol intermediate compound is triggered by the radical OH attack on the ortho position of 4-NP. However, the ortho position at 4-NP is stabilized by the hydroxyl group at 4-NP. Hence, the attack from the OH radicals will incline to the less stable position of the metha until 4-nitrocatechol is formed. This compound is an intermediate compound that is less stable, making it easily degradable into lower molecules [39]. The degradation that occurred at 4-NP in this study did not reach a breakdown to lower components such as CO_2 and H_2O . However, the breakdown of the 4-NP component only breaks the benzene group. This might occur due to the production of OH radicals which are still lacking and the short time of electrolysis.



Figure 7. Proposed electrochemical degradation pathway of 4-NP on Ti/TiO₂-NiO electrode



Figure 8. (a) COD test from the degradation of 4-NP 10 mg L^{-1} at pH 11.0, (b) repeatability test of Ti/TiO₂-NiO electrode for degradation 4-NP 10 mg L^{-1} at pH 11.0

The breakdown of the 4-NP compound was also confirmed by COD analysis. COD is usually used as an indicator of organic degradation in the wastewater. It was observed that the presence of electrolysis using Ti/TiO₂-NiO electrodes was able to reduce the COD value to 30.12%. This shows that the mineralization process from 4-NP becomes a lower molecular weight compound. In addition, in this study, the stability of Ti/TiO₂-NiO electrodes was examined in 4-NP degradation. The results of the electrode stability testing are shown in **Figure 8.** The stability test was carried out in a 10 mg/L 4-NP solution of 20 measurements. The results indicate that the electrodes have good measurement stability in the measurement range because the RSD value of the measurement is smaller than 11.31% as the percentage of its RSD Horwitz.

CONCLUSION

Ti/TiO₂-NiO electrodes were successfully made in this study through thermal decomposition methods and have been used as electrodes for the degradation of 4-NP in an aqueous medium. Under these optimal conditions, 4-NP removal using Ti/TiO₂-NiO electrode of approximately more than 95% was reached with a degradation rate of 0.039 min⁻¹. The degradation of the 4-NP compound was confirmed by the decrease concentration and COD value. This shows that Ti/TiO₂-NiO electrodes can be effectively used as electrodes in 4-NP degradation, although this notion still requires further study, especially into the effect of the addition of electron receptor compounds such as H₂O₂. From this study, the mechanism of 4-NP degradation does not occur directly but the degradation can occour through the formation of OH radicals produced from the breakdown of H₂O₂ compounds.

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Highlights

- Ti/TiO₂-NiO electrodes were designed for electrochemical 4nitrophenol degradation
- It exhibited high catalytic degradation with the constant rate 0.0373 min⁻¹
- Mechanism for the rate of degradation of 4-NP is proposed
- The method is promising for real water treatment