Effects of Synthesis Ni Doped TiO$_2$ on Photocatalytic Degradation Process

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Abstract

Titanium is oropoxide, Ethanol, Acetic acid and nickel chloride hexahydrate were used as reagents. The objectives of this study is to synthesize TiO$_2$ and Ni doped TiO$_2$ powders by using reflux sol-gel method and to compare the removal percentage of azo dye solution on two synthesis powders suspension by using photocatalytic degradation process. And then the powders are characterized by SEM parameter. The photocatalytic degradation process not only decolorized the azo dyes but also mineralized the intermediate products completely using in the UV-Vis spectrophotometer. The kinetics of photocatalytic degradation was observed to follow the pseudo-first order according to Langmuir-Hinshelwood kinetics model.

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INTRODUCTION

In several years, various kinds of organic pollutants to be decomposed by using TiO$_2$ nanoparticles extensively because TiO$_2$ particles had a lot of efficiency of high oxidative power, non-toxicity, photostability and water insoluble properties under most conditions [10]. Moreover, TiO$_2$ photocatalysts were low prices, chemical stability and no toxicity and which can be completely decolorization and immobilization of many toxic organic pollutants [8], TiO$_2$ modification has been justified to various kinds of approaches by metal-ion doped-TiO$_2$ and non-metal doped-TiO$_2$. By using transition metal for metal-ion doped-TiO$_2$ are Cu, Co, Ni, Cr, Mn, Mo, Nb, V, Fe, Ru, Au, Ag and Pt and non-metal doped-TiO$_2$ are N, S, C, B, P, I and F [11]. A transition metal ion of doped-TiO$_2$ has been experiment by improving photocatalytic activity of semiconductor oxides [3].

Nickel is one of transition elements used to modify the titania surface. The effects of Ni$^{2+}$ on the photocatalytic properties of TiO$_2$ have been investigated by several authors [7]. More importantly, the existence of Ni$^{2+}$ greatly suppressed recombination of electron–hole pairs on the surface of the photocatalyst [6]. On the other hand, low valence Ni$^{2+}$ ion dopant improves the photocatalytic activity of certain semiconductor photocatalyst [5,9]. However, the photocatalytic activity of the prepared metal-doped TiO$_2$ photocatalysts depends strongly on the species and concentration of the dopant ion [11]. TiO$_2$ mediated heterogeneous photocatalysis conducted potentially advantages by improving ambient conditions and many organic pollutants of harmless products of CO$_2$, H$_2$O and mineral acids by perfect mineralization [4]. In this study is to decolorized azo dyes by different volume amount of doped-TiO$_2$ and compare the effects of this photocatalysts under sunlight irradiation.

MATERIALS AND METHODS

Chemicals:

Titanium isopropoxide (Ti(OC$_3$H$_7$)$_3$), ethanol(C$_2$H$_5$OH), acetic acid(CH$_3$COOH), nickel chloride hexahydrate (NiCl$_2$.6H$_2$O) and Acid orange 7 (C$_{18}$H$_{11}$N$_5$NaO$_2$S) were purchased.

Synthesis method:

The doped TiO$_2$ photocatalysts were prepared by calcination of synthesis TiO$_2$ product with nickel chloride hexahydrate (NiCl$_2$.6H$_2$O) as precursor for Ni-doped TiO$_2$. 10ml Ti(OC$_3$H$_7$)$_3$ and 17ml C$_2$H$_5$OH are mixed and stirring well. After one hour, 1ml of distilled water was added drop by drop into this solution. 20ml volume ratio of 0.5 mole precursor was added at three hour of synthesis solution and continues stirring one hour by vigorously. And then, 1.7ml of CH$_3$COOH is added and 1min stirred with this solution. Moreover, the solution is changed and reflux three hours for becomes sol-gel type. After reflux time, the sol-gel are filtered and dried in
oven at 70°C for 24 hours. Finally, the doped TiO₂-catalyst particles were obtained through calcination in a muffle furnace at 500°C for 2 hours.

**Photocatalytic procedure:**

The photocatalytic degradation experiments of 30mg/l AO7 solutions were investigated in under sunlight irradiation in 0.3g of synthesis and doped TiO₂ suspensions. The 500ml of AO7 solutions were prepared from stock solution by dilution with ultra-pure water. The experiments are done for 6 hours and 20ml of water samples were collected at 0, 0.5, 1, 1.5, 2, 3, 4, 5 and 6 hours. To obtain the clear water samples by using 0.45 μm membrane filter paper was used for collecting all samples to remove the synthesis TiO₂ and synthesis doped TiO₂ particles.

**RESULTS AND DISCUSSION**

**SEM analysis obtained results:**

Figure 1 (a) and (b) shown scanning electron microscopy observation of synthesis TiO₂ and Ni-doped TiO₂ powders. The aggregate formed by the emulsifiantgelation technology has an average size in the range of 1 μm. And then the aggregate has a spherical shape with an average diameter of around 200 to 300 nm can be observed for both synthesis powders.

![SEM images](image1.png)

Fig. 1: SEM of (a) synthesis TiO₂ and (b) Ni-doped TiO₂ powders.

**Photocatalytic activity of AO7 on Ni-doped-TiO₂ suspensions:**

Figure 2 illustrated that the effect of photocatalytic degradation activity of 30mg/l Acid Orange 7 by synthesis TiO₂ and Ni-doped TiO₂ suspensions. In this results, more adsorption efficiency in nickel doped TiO₂ compared with synthesis TiO₂. The photodegradation percent of synthesis TiO₂ and Ni-doped TiO₂ are 58% and 66%, respectively. Moreover, Ni²⁺ activated an important role in trapping the electrons and helps in charge separation, therefore photocatalytic activity is comparatively good.

**Kinetics analysis for the photocatalytic degradation of single and binary azo dye solutions:**

Table 1 was shown the k_{app} values for the photocatalytic degradation of synthesis TiO₂ and Ni-doped TiO₂ powders. The Langmuir-Hinshelwood model mentioned equivalent to concern with the pseudo first-order kinetics of photocatalytic degradation of basic azo dyes [2]. The k_{app} value for synthesis TiO₂ and Ni-doped TiO₂ were 0.0024 and 0.0025 respectively. Therefore, the value of synthesis Ni-doped TiO₂ is larger than that of synthesis TiO₂ under approximate conditions. The R² of synthesis TiO₂ is 0.8275 and Ni-doped TiO₂ is 0.9975.
Fig. 2: (a) Photocatalytic degradation activity of AO7 solutions by synthesis TiO₂ and Ni-doped TiO₂ suspensions.

Table 1: Values of $k_{app}$ for the photodegradation degradation of 30mg/l AO7 by synthesis TiO₂ and Ni-doped TiO₂ suspensions.

<table>
<thead>
<tr>
<th></th>
<th>Synthesis TiO₂</th>
<th>Synthesis Ni-doped TiO₂</th>
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<tbody>
<tr>
<td>$k_{app}$</td>
<td>0.0024</td>
<td>0.0025</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.8297</td>
<td>0.9975</td>
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</tbody>
</table>

Conclusion:

Both synthesis powders have spherical shape and average size are around 200-300nm. But the color removal percentage of Ni-doped TiO₂ is more than synthesis TiO₂ in photocatalytic degradation process. And then, the kinetics value of Ni-doped TiO₂ is also larger than synthesis TiO₂.

REFERENCES