Degradation of Semiconductor Manufacturing Wastewater by Using a Novel Magnetic Composite TiO$_2$/Fe$_3$O$_4$ Photoreactor Design

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1. Introduction

In the typical semiconductor manufacturing processes, a large amount of IPA is used for wafer cleaning. The wafer cleaning processes invariably generate a large quantity of wastewater that contains refractory and complex organic compounds. Not only do these organic compounds pose direct or indirect harm to the liver, kidney, central nervous system, and skin, some of them have already been verified as carcinogen, teratogenic agent, and gene mutagen for humans. Traditional wastewater treatment approaches involving physical-chemical decomposition or microorganisms have shown only limited efficiencies [1]. Many advanced oxidation processes (AOPs) have been extensively utilized for the decomposition of hazardous or recalcitrant pollutants in the environment. In recent years, TiO$_2$ has attracted much attention because of the low price and steady and high photocatalytic activation [1–4]. However, requirement of using UV light to activate TiO$_2$ photocatalyst and difficulty to recover the photocatalyst are still major limitation for degradation of environmental pollutants [5, 6]. There are many types of conventional methods to modify quality of photocatalyst. One of them is TiO$_2$ photocatalyst doped by the transition metal [7–22]. It makes the defect of the structure of TiO$_2$ and produces the lower energy gap. Therefore, just less energy reacts with O$_2$ and H$_2$O in the environment to form the excited electron and holes. As a consequence, the absorbed spectrum of TiO$_2$ can shift into the region of visible light. V, Fe, Cr, Ni, Cu, and other transition metals are well-known to be doped into TiO$_2$ thin film to shift the band gap to visible light. Producing visible-light-activated TiO$_2$ powder for easy recovery can be beneficial. Iron enhances TiO$_2$ visible light absorption and thus increases its photocatalytic activity. Previous researches have reported that iron-based nanoparticles have been superparamagnetic [1, 18, 23, 24] and have been coated with organic polymers such as porphyrin and other dyes [6, 25, 26] or other inorganic elements such as N and H [27–29] and other methods [29, 30]. This research uses sol-gel method to add Fe$_3$O$_4$ during TiO$_2$ synthesis and then uses visible-light-irradiated TiO$_2$/Fe$_3$O$_4$ to conduct photodegradation effect on IPA. The photodegradation efficiency of IPA and
the recovery rate of photocatalyst will be also evaluated in this study.

2. Experimental/Materials and Methods

2.1. Preparation of Photocatalyst. In this study, the TiO$_2$/Fe$_3$O$_4$ complex was prepared using the modified sol-gel method [4]. The sol-gel process is one of the versatile methods to prepare high-pure and nanosize materials shaped as powders or coatings. This approach does not need complicated instruments such as chemical vapor deposition. It provides a simple and easy method to synthesize nano-size photocatalysts. First, soluble TiO$_2$ precursor powder was prepared using a mixture of tetraisopropyl orthotitanate (Ti(OC$_3$H$_7$)$_4$) (TTIP, >98%, Merck Co.), 2-propanol (>99.7%, JT. Baker), and acetic acid (>99.9%, JT. Baker). Then, the mixed solutions were stirred for 24 h and dried at 105°C followed by 150°C for 1 h, respectively. The dried gel was then pulverized into powder and calcinated in the high-temperature oven. The parameters employed to control the preparation of the catalyst include 2-propanol, acetic acid (TTIP was fixed), calcinations time, and calcinations temperature. The orthogonal arrays in the design of the experimental method proposed by Taguchi were adopted to conduct the multiple-factor experiment. Second, the above-prepared TiO$_2$ powder was directly mixed with iron oxide (Fe$_3$O$_4$, >98%, Aldrich) and Fe$_3$O$_4$/TiO$_2$ at the designed molar ratio of 0.1. Then, the mixed solutions were stirred for 1 h and dried at 105°C for 1 h. The conversion rate of IPA in this experiment was employed to identify the optimal conditions for assembly. The reactor containing TiO$_2$/Fe$_3$O$_4$ complexes was irradiated with 419 nm fluorescent lamps to undergo the batch photocatalytic degradation experiment.

2.2. Photoelectrocatalytic Procedure. The liquid-phase photoelectrocatalytic system consisted of 16 VFLs (Rayonet Model RPR 100 Photochemistry Reactor, the Southern New England Ultraviolet Company, fluorescent lamps $\lambda_{\text{max}} = 419$ nm, intensity = 724 lx), a completely mixing reactor, and an air compressor for aeration and stirring use, and a peristaltic pump was used to draw sample into the reactor for the continuous refluxing batch experiments and the flow rate controlled at 105°C followed by 150°C for 1 h, respectively. The dried gel was then pulverized into powder and calcinated in the high-temperature oven. The parameters employed to control the preparation of the catalyst include 2-propanol, acetic acid (TTIP was fixed), calcinations time, and calcinations temperature. The orthogonal arrays in the design of the experimental method proposed by Taguchi were adopted to conduct the multiple-factor experiment and obtain the best combination of conditions for experimental photocatalytic conversion of IPA. The four parameters of various levels yield 9 different combinations as summarized in the L$_9$ orthogonal array table. Different photocatalysts were prepared according to different combinations of controlling factors for conducting the heterogeneous photocatalytic reactions to obtain the conversion rates of IPA. The IPA conversion rates thus obtained were then statistically analyzed by the F test to determine the significance and variability of each factor. The result showed that, among the factors, calcinations temperature had the greatest effect on conversion rate of IPA in the photocatalysis system (42.06%), followed by calcinations time (27.14%), the amount of 2-propanol (14.86%), and, finally, the amount of acetic acid (14.67%). In general, the effect of calcination temperature was more significant due to its function in removing impurities and increasing crystal strength. Table 1 shows the contributions and major effects of different parameters. The optimal preparation condition of TiO$_2$ catalyst was achieved under water 2-propanol of 0.08 mol, acetic acid of 0.32 mol (i.e., TTIP/2-proanol/acetic acid with a molar ratio of 1:2:8), calcinations temperature of 500°C, and calcinations time of 90 min. The TiO$_2$ was prepared at the above optimal experimental conditions. Then, the above prepared TiO$_2$ powder was directly mixed with Fe$_3$O$_4$ and Fe$_3$O$_4$/TiO$_2$ at the designed molar ratio of 0.1, and the mixed solutions were stirred for 1 h and dried at 105°C for 1 h. The solid was calcinated in an atmospheric oven heated to 200°C at

![Figure 1: Schematic diagram of continuous photocatalytic degradation system.](image-url)
Table 1: Response of parameters in L9 table.

<table>
<thead>
<tr>
<th>Factors</th>
<th>2-propanol (mol)</th>
<th>Acetic acid (mol)</th>
<th>Calcination temperature (°C)</th>
<th>Calcination time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Level 1</td>
<td>61.89</td>
<td>48.52</td>
<td>52.98</td>
<td>67.51</td>
</tr>
<tr>
<td>Level 2</td>
<td>47.54</td>
<td>62.11</td>
<td>36.67</td>
<td>40.64</td>
</tr>
<tr>
<td>Level 3</td>
<td>59.19</td>
<td>58.03</td>
<td>78.64</td>
<td>60.08</td>
</tr>
<tr>
<td>Main effect</td>
<td>14.86</td>
<td>14.67</td>
<td>42.06</td>
<td>27.14</td>
</tr>
</tbody>
</table>

3.2. Properties Analysis of Photocatalysts. The photocatalyst prepared by the modified sol-gel method under the optimal conditions described above and the magnetism was tested and is shown in Figures 2, 3, and 4. As can be seen, the pure Fe3O4 particles and TiO2/Fe3O4 composite catalyst also had good magnetism. The magnetization curve of TiO2/Fe3O4 composite catalyst was measured with Superconducting Quantum Interference Device Magnetometer (SQUID; SQUID-PMS5, Quantum Design Corp.), and Figure 5 illustrates the saturation magnetization intensity of TiO2/Fe3O4 composite catalyst was 5.8 emu/g. The field-emission scanning electron micrographs (FE-SEM, JSM-6700F, JEOL, Japan) of TiO2/Fe3O4 composite catalyst were shown in Figure 6, and they clearly displayed that the particle was little irregular and the size was about 20–40 nm. Anatase TiO2 containing Fe3O4 was obtained and analyzed by the X-ray diffractometer (XRD) and compared with the JCPDS database (no. 84-1286 and 89-4319) (Figure 7). The X-ray diffractometer (XRD, MAC MXIII) was used to examine the crystals form.

3.3. Adsorption Effect. In this study, the adsorption ability of the TiO2/Fe3O4 composite catalyst has been studied at varied pH (4, 7, and 10) with 30 mg L\(^{-1}\) IPA without any irradiation at temperature of 25°C in the reaction chamber for 240 minutes. The adsorption ability for the TiO2/Fe3O4 composite catalyst was weak under alkaline and neutral conditions but not significantly different. Because all of the adsorption rates were less than 1%, the effect of adsorption was not taken into consideration in the following experiments, which did not affect the interpretation of the data acquired.

3.4. Photocatalytic Tests. Because the photolytic efficiency of UV irradiation treated with IPA was less than 2% in 3 replicates test, therefore the part experiment was not taken into comparing in the subsequent experiments. The photoactivity indicator of the TiO2/Fe3O4 composite catalyst was investigated by the conversion rate of IPA. The 2.0 g TiO2/Fe3O4 composite catalyst was used to react with 30 mg L\(^{-1}\) IPA under 3.0 mW cm\(^{-2}\), 365 nm UV light (UV-A), 724 lx VFL at pH 7 for 240 min. The results are illustrated in Figure 8, and the destruction removal efficiency (DRE) of the TiO2/Fe3O4 composite catalyst on the conversion of IPA was higher than the TiO2 catalyst alone. Evidence reveals that the system of the TiO2/Fe3O4 complexes has significantly high efficiency of photocatalytic degradation than TiO2 only.

From the experimental data, we could find and understand that the TiO2 and TiO2/Fe3O4 composites had good performance under UV irradiation because UV light was with higher energy, but this experiment verified that visible fluorescent light could activate the photocatalytic activity of TiO2/Fe3O4 particles as did ultraviolet A light. The result showed that the TiO2/Fe3O4 composite catalyst also had good destruction rate for IPA under visible light, and this evidence revealed that the system of the TiO2/Fe3O4 composite catalyst could be used to treat organic pollutants in practical wastewater treatment factories.

3.5. pH Effect. Although there was no significant variation of adsorption experiments under different pH values, there
were obvious variations in the photocatalytic reactions. In general, the yield of hydroxyl radicals in the photocatalytic reaction increases with increasing pH of the aqueous solution. However, the distribution ratios of the intermediates produced in the solution were directly related to the pH values. Moreover, the pH value alters the electrical behavior on the surface of the photocatalyst leading to changes in the absorption and desorption properties and capabilities of the intermediates produced by the catalyst. Therefore, the control of pH during the operation had significant impact on the efficiency of the overall treatment.

The pHzpc value of TiO2 is 6.4. Therefore, the TiO2 surface carries a positive charge at pH below 6.4. However, more and more oxygen ions dissociate from the TiO2 surface at pH above 6.4, causing a negative charge to develop on the catalyst surface. The substances formerly attached to the catalyst surface as a result of electrostatic adsorption begin to leave the catalyst under the influence of electric repulsion between the substances and the catalyst, thus lowering the oxidation/reduction rate of the reactants. Therefore, the ionic reactants are more affected by the pH of the environment due to electrostatic interaction. Figure 9 illustrates the destruction removal efficiency of IPA under the VFL irradiation for 240 minutes of photocatalytic reaction. As can
be seen, the removal rate of IPA was higher under basic conditions, and the result coincided with previous studies [32].

3.6. Effect of Addition of Photocatalyst. The objective of the present study was to identify the optimal quantity of the TiO\textsubscript{2}/Fe\textsubscript{3}O\textsubscript{4} composite catalyst added according to economic consideration. This part of the experiment was carried out under the following conditions: initial IPA concentration of 30 mg L\textsuperscript{-1}, pH 7, temperature of 25°C, and VFL for 240 min. The variations in DRE thus obtained are illustrated in Figure 10. As can be seen, when the photocatalyst added was increased from 1 g to 5 g, the DRE was improved from 46% to 88%. However, when the amount of the TiO\textsubscript{2}/Fe\textsubscript{3}O\textsubscript{4} composite catalyst added was increased from 5 g to 10 g, the DRE was reduced. It was speculated that excessive amount of the TiO\textsubscript{2}/Fe\textsubscript{3}O\textsubscript{4} photocatalyst added to the solution caused shielding of the light. Thus, both the light path and amount of TiO\textsubscript{2}/Fe\textsubscript{3}O\textsubscript{4} photocatalyst available for visible light irradiation were reduced, resulting in a decrease in overall treatment efficiency. At the same time, the recovery rate of photocatalyst could reach to 99.8% as we recollected easily from recycled water using magnet (shown in Figure 11). It is also illustrated that the system of TiO\textsubscript{2}/Fe\textsubscript{3}O\textsubscript{4} has significant efficiency of photodegradation under visible light irradiation and can be used and recycled in the practical wastewater treatment factories in the future.

4. Conclusions

Various dopants have been used for TiO\textsubscript{2} to absorb visible light. Fe\textsubscript{3}O\textsubscript{4} was chosen and added during the preparation of TiO\textsubscript{2} photocatalyst using sol-gel method that made TiO\textsubscript{2} photocatalytic activity be activated by visible light. In this study, the synthesized TiO\textsubscript{2}/Fe\textsubscript{3}O\textsubscript{4} can be activated by irradiation of UV-A and VFL. No significant photocatalytic activity was lost after being recollected from water using magnet for reusing. TiO\textsubscript{2}/Fe\textsubscript{3}O\textsubscript{4} also demonstrated the DRE of IPA under VFL and resolved TiO\textsubscript{2}/Fe\textsubscript{3}O\textsubscript{4} recovery problem when it was used in the practical wastewater treatment factories. In addition, The prepared TiO\textsubscript{2}/Fe\textsubscript{3}O\textsubscript{4} photocatalyst was identified as anatase, and particle size was about 20~40 nm formed by XRD and FE-SEM. In the photodegradation experiments, the results indicated that 40~88% DRE reached at different amounts of TiO\textsubscript{2}/Fe\textsubscript{3}O\textsubscript{4}, and the best addition amount was 5 g TiO\textsubscript{2}/Fe\textsubscript{3}O\textsubscript{4} under pH 10.

References


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