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Research Article

Synthesis and Bactericidal Ability of TiO₂ and Ag-TiO₂ Prepared by Coprecipitation Method

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Preparation of photocatalysts of TiO₂ and Ag-TiO₂ was carried out by coprecipitation method. The prepared photocatalysts were characterized by X-ray diffraction (XRD), SEM, EDX, and XRF analysis. The disinfection of E. coli, a model indicator organism for the safe water supply, was investigated by using TiO₂ and Ag-TiO₂ under different light sources. The treatment efficacy for the inactivation of E. coli would be UV/Ag-TiO₂; visible/Ag-TiO₂; dark/Ag-TiO₂; UV (all 100%) > UV/TiO₂ (99%) > visible/TiO₂ (96%) > dark/TiO₂ (87%) > visible (23%) > dark (19%). The order of disinfection efficiency by their corresponding kinetic initial apparent rate constants, k_app, (min⁻¹) would be UV/Ag-TiO₂; visible/Ag-TiO₂ (both 6.67) > UV (6.6) > dark/Ag-TiO₂ (6.56) > UV/TiO₂ (1.62) > visible/TiO₂ (1.08) > dark/TiO₂ (0.7) > visible (0.28) > dark (0.03). The application of TiO₂ doped with silver strongly improved the ability of disinfection treatment. The study of mineralization of E. coli by measurement of TOC (total organic carbon) removal percentage showed that the visible light may effectively be applied for the disinfection unit of water and wastewater treatment system by using photocatalysts of Ag-TiO₂.

1. Introduction

Increasing demand and shortage of satisfactory clean water supplies due to the rapid development of industrialization, population growth, and serious droughts have become a global issue [1–3]. It is estimated that around 1.2 billion people lack access to safe drinking water, 2.6 billion have little or no sanitation, and millions of people died of severe waterborne diseases annually [3, 4]. Therefore, the quality of drinking water is becoming more and more of a concern worldwide. For suppressing the worsening of clean water shortage, disinfection development of advanced water treatment technologies with low cost and high efficiency to treat wastewater is also desirable. Pathogens are disease-causing organisms that grow and multiply within the host and excreted in human feces. Pathogens associated with water include bacteria, viruses, protozoa, and helminthes [5]. The microbiological standards for water and wastewater treatment system in their final disinfection treatment unit use coliform bacteria (typically Escherichia coli or E. coli) as indicator organisms whose presence suggests that water is fecal contaminated. The final disinfection step to kill any remaining pathogenic organisms for water and wastewater treatment system includes some commonly used technologies, such as chlorination, ozonation, and UV irradiation. Chlorination has been the most commonly and widely used disinfection process. The disinfected byproducts generated from chlorination are mutagenic and carcinogenic to human health [5–7], while ozonation, or UV radiation may be too costly and can only be used as primary disinfectant because they cannot ensure a detectable residual [1, 8].

Heterogeneous photocatalysis has recently emerged as an alternative technology of advanced oxidation processes (AOP) for bacteria inactivation [9–16] and organic pollutants oxidation [17–29]. Out of the various semiconductor photocatalysts used, TiO₂ has been found to be the most suitable because of its nontoxic, insoluble, inexpensive, stable, and its high production of oxidative hydroxyl radicals (·OH). But the rapid recombination of electron-hole pair limits the efficiency of TiO₂. It is experimentally found that Ag particles in Ag doped TiO₂ increase the bactericidal efficiency of TiO₂ by acting as electron traps [1, 30–34].
Figure 1: SEM micrograph of Ag-TiO$_2$ sintering at 550°C (×6.0k).

The aim of this work was the preparation of TiO$_2$ and Ag doped TiO$_2$ (Ag-TiO$_2$) by the simple coprecipitation method. The prepared photocatalysts were characterized by X-ray diffraction (XRD), SEM, EDX, and XRF analysis. The photocatalytic inactivation and disinfection of $E$. coli, one of the most common gram-negative model bacteria, using prepared TiO$_2$ and Ag-TiO$_2$ under irradiation of different light sources were studied and compared. The mineralization of $E$. coli by the study of TOC (total organic carbon) removal percentage was also investigated by different light sources.

2. Experimental

2.1. Materials. All chemicals used such as Ti(SO)$_4$, urea, or silver nitrate were of reagent grade (SHOWA Chemical Co., LTD., Japan or Ruenn-Jye Tech. Corp., Taiwan). The photocatalytic antibacterial activities of the samples were evaluated using $E$. coli as an indicator bacterium. $E$. coli (BCRC10316) was obtained from FIRDI, Taiwan. Nutrient broth (NB, Pronadisa, Lab conda S.A.) and agar (American bacteriological agar; Pronadisa, Lab conda S.A.) were used for the liquid culture medium and solid culture medium of bacteria, respectively.

2.2. Preparation of TiO$_2$ and Ag-TiO$_2$. For the preparation of Ag-TiO$_2$ powder, 75 g of urea was first dissolved into 400 mL DI-water. Then add 46 mL of Ti(SO)$_4$ and 0.169 g of AgNO$_3$ into the bottle on the oil bath and uniformly mixed. Reactions were carried out for 24 h at 80°C by continuously magnetic stirring and heating. After cooling to room temperature, the separation of solid and solution was obtained by centrifugal filtration. The solids were washed by DI-water until pH of the washing water reached neutral. The solids were filtered again and removed to the oven for drying at 70°C and 24 h. By grinding, the powder was then calcined at 550°C for 4 h. The Ag-TiO$_2$ was obtained with Ag:Ti = 1:99 (molar ratio). To prepare TiO$_2$, the same procedure was repeated without the addition of silver nitrate.

2.3. Characterization of Prepared Photocatalysts. Structure characterization of as prepared photocatalysts was performed by means of XRD (XRD-6000, Shimadzu, Japan).
Figure 5: Inactivation effect of E. coli by visible light irradiation using TiO$_2$ (i) (0 min.) and (ii) (15 min.) and Ag-TiO$_2$ (iii) and (iv) as photocatalysts.

Figure 6: R percentage versus irradiation time of different light sources using TiO$_2$ as photocatalysts.

Figure 7: R percentage versus irradiation time of different light sources using Ag-TiO$_2$ as photocatalysts.

2.4. Inactivation of E. coli. The antibacterial properties of E. coli by using photocatalysts were studied under the following process. (1) Preparation of liquid growth medium of nutrient broth (NB): add 0.8 g of NB and 100 mL Di-water into 250 mL of flask and sterilized under autoclave for 20 minutes. (2) Preparation of solid medium: mix 0.8 g NB, 1.5 g agar, and 100 mL DI-water and sterilized under autoclave at 121$^\circ$C for 20 minutes and then cool until 50$^\circ$C. Pour the contents into petri dishes to form solid medium. (3) Add E. coli from FIRDI onto petri dishes and incubated at 37$^\circ$C for 2 days. (4) Remove E. coli from the surface of solid medium from

with Cu K$\alpha$ radiation. Morphology of Ag-TiO$_2$ was investigated by SEM (Scanning electron microscope, S-3000N, Hitachi, Japan). EDX (Energy dispersive X-ray spectroscopy) used indicates the presence of silver. The chemical compositions of the particles were analyzed by XRF (X-ray fluorescence, XEPOS/XEP01, Spectro Co., Germany).
Figure 8: Inactivation effect of E. coli by irradiation of different light sources (UV (i) (0 min.) and (ii) (15 min.) and visible (iii) and (iv) and dark (v) and (vi)) using Ag-TiO₂ as photocatalysts.

(3) when cooled and inoculate onto (1) by the same cultural procedure as (3). (5) Dilution of E. coli from (4): add 1 mL of inoculated E. coli from liquid culture medium of NB and into a clean test tube containing 9 mL of sterilized water. Add 0.01 g of Ag-TiO₂ into the prepared test tube. The test tube was incubated for 24 h at 37°C, and the numbers of viable cells of bacterial colonies (CFU/mL, colonies forming units per milliliter) were visually identified and counted. Repeat the serial dilution by 10¹, 10², 10³, 10⁴, 10⁵, and 10⁶. The best dilution for the E. coli bactericidal effect by photocatalysts would be 10⁶ for all the following inactivation experiments.

(6) The inactivation of E. coli bacteria: the bactericidal studies by the photocatalysts were carried out under the irradiation of visible light (Philips, Poland, 9 watts), UV light (UV-C, Philips, Poland, 9 watts), and no light. The distance between the light and the top of test tube remains 30 cm and fully covered and protected on the outside. Then lay the setup into the laminar flow cabinet and investigate the inactivation experiments. The similar procedure was applied as (5) by using the dosages of 0.01 g/10 mL of TiO₂ or Ag-TiO₂. The dilution chosen would be 10⁶, and sampling time for each experiment would be 0, 15, 45, 90, 135, and 180 minutes. Samples were all plated in triplicate, and the counts on the three plates were averaged. Control experiments were also conducted in the absence of the photocatalysts.

The inactivation efficiency R(%) of E. coli as model bacteria by the prepared photocatalysts of TiO₂ and Ag-TiO₂ were calculated by the following equation:

\[ R(\%) = \frac{(C₀ - C)}{C₀} \times 100\%, \]

where R(%) is the inactivation efficiency or viable cells inactivated or removed percentages. C₀ is initial CFU/mL, and C is final CFU/mL.

3. Results and Discussion

3.1. Catalyst Characterization. Ag-TiO₂ after 550°C sintering was characterized by the SEM. The micrographs taken at 6000-times magnification are shown in Figure 1. It is found that the dope of silver is not very obvious and the aggregation of tiny TiO₂ particles occurred. The average particle size was found to be about 2.5 μm from the figure. The XRD patterns of TiO₂ and Ag-TiO₂ as shown in Figure 2 almost coincide and thus suggest that the silver is well dispersed on the TiO₂ surface. Anatase type structure is obtained for both prepared TiO₂ and Ag-TiO₂. Figure 2 also shows the XRD patterns of Ag-TiO₂ annealed at different temperatures and all exhibited anatase without rutile. With
increasing temperature of calcination, the intensities of the TiO\textsubscript{2} peaks are increased. Therefore, the photocatalysts of Ag-TiO\textsubscript{2} used for the inactivation of \textit{E. coli} will be prepared by 550°C sintering. From Figure 2, there is only TiO\textsubscript{2} in the anatase form and no peaks of Ag were observed. It can be explained that the amount of Ag is too little to be appeared on the patterns. Figure 3 is the EDX diagram of Ag-TiO\textsubscript{2} which indicates the presence of silver on the prepared photocatalysts.

The compositions of the prepared Ag-TiO\textsubscript{2} were determined by the analysis of XRF. The result was shown in Table 1. It indicates that silver exists and composition was very close to the predetermined value, that is, Ag : Ti = 1 : 99 (molar).

3.2. Inactivation of \textit{E. coli}

3.2.1. Comparison between TiO\textsubscript{2} and Ag-TiO\textsubscript{2} under Visible Light. Figures 4 and 5 show the inactivation of \textit{E. coli} under the irradiation of visible light by using photocatalysts of TiO\textsubscript{2} or Ag-TiO\textsubscript{2}. It is quite clear that Ag doped TiO\textsubscript{2} improves very obviously the antibacterial activities of \textit{E. coli} on both inactivation efficiency (R\%) and rate of reaction. It takes about 15 minutes to reach 99% inactivation for Ag-TiO\textsubscript{2} and 180 minutes of 90% for TiO\textsubscript{2}.

According to the kinetic Langmuir-Hinshelwood model [21]:

\[
r = -\frac{dC}{dt} = \frac{(k_rKC)}{(1 + KC)},
\]

(2)

During the initial stage of reaction, concentration of \textit{E. coli} is high, the reaction becomes zero order, that is,

\[
r = -\frac{dC}{dt} = k_r.
\]

(3)

Therefore,

\[
(C - C_0) = -k_r t \quad \text{or} \quad R\% = \left(\frac{C_0 - C}{C_0}\right) \left(\frac{k_r}{C_0}\right) t = k_{app} t,
\]

(4)

where \( r \) is the rate of \textit{E. coli} inactivation, \( C_0 \) is the initial concentration of \textit{E. coli}, \( C \) is the concentration of \textit{E. coli} during the initial stage of reaction (straight-line region) at time \( t \), \( k_r \) is the reaction rate constant, \( k \) is the adsorption coefficient of \textit{E. coli} onto particle, and \( k_{app} \) is the apparent rate constants (min\textsuperscript{-1}).
Table 1: XRF of prepared Ag-TiO₂.

<table>
<thead>
<tr>
<th>Components</th>
<th>Conc.: mol%</th>
<th>STD-DEV</th>
<th>Intens.: cps/μA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti (titanium)</td>
<td>97.83</td>
<td>0.08</td>
<td>138.140</td>
</tr>
<tr>
<td>V (vanadium)</td>
<td>1.2</td>
<td>0.07</td>
<td>2.533</td>
</tr>
<tr>
<td>Ag (silver)</td>
<td>0.81</td>
<td>0.03</td>
<td>3.575</td>
</tr>
<tr>
<td>Fe (iron)</td>
<td>0.16</td>
<td>0.03</td>
<td>0.248</td>
</tr>
</tbody>
</table>

Table 2: Values of $R$ (%) and $k_{app}$ by using different light sources and different photocatalysts of TiO₂ and Ag-TiO₂ or light only.

<table>
<thead>
<tr>
<th>Light Sources</th>
<th>$R$ (%)</th>
<th>$k_{app}$ (min⁻¹)</th>
<th>Ag-TiO₂</th>
<th>$R$ (%)</th>
<th>$k_{app}$ (min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dark</td>
<td>19%</td>
<td>0.03</td>
<td>Dark</td>
<td>19.46%</td>
<td>0.03</td>
</tr>
<tr>
<td>Visible</td>
<td>23%</td>
<td>0.28</td>
<td>Visible</td>
<td>23.14%</td>
<td>0.28</td>
</tr>
<tr>
<td>Dark + TiO₂</td>
<td>87%</td>
<td>0.7</td>
<td>UV</td>
<td>100%</td>
<td>1.67</td>
</tr>
<tr>
<td>Visible + TiO₂</td>
<td>96%</td>
<td>1.08</td>
<td>Dark + Ag-TiO₂</td>
<td>100%</td>
<td>6.56</td>
</tr>
<tr>
<td>UV</td>
<td>99%</td>
<td>1.56</td>
<td>Visible + Ag-TiO₂</td>
<td>100%</td>
<td>6.67</td>
</tr>
<tr>
<td>UV+TiO₂</td>
<td>100%</td>
<td>2.22</td>
<td>UV + Ag-TiO₂</td>
<td>100%</td>
<td>6.67</td>
</tr>
</tbody>
</table>

4. Conclusions

(1) Photocatalysts of TiO₂ and Ag-TiO₂ were successfully prepared by coprecipitation method annealed at 550°C;

(2) the composition of Ag-TiO₂ prepared is about Ag:Ti = 1:99 (molar), and particle size is 0.25 μm;

(3) silver-deposited TiO₂ photocatalysts enhanced the inactivation of E. coli by visible irradiation when compared to that by using TiO₂. The similar 100% of high antibactericidal efficiencies and six times of rate of reaction compared to the usage of TiO₂ were obtained for either using visible light or UV light or even no light irradiation by the application of Ag-TiO₂;

(4) the study of mineralization of E. coli shows that better results of TOC removal percentage obtained for visible light application than the irradiation of UV light;

(5) the visible light may effectively be applied for the disinfection unit of water and wastewater treatment system by using photocatalysts of Ag-TiO₂.

References


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