Photocatalytic degradation of Trimethoprim using S-TiO$_2$ and Ru/WO$_3$/ZrO$_2$ immobilized on reusable fixed plates

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Abstract

In this study, photocatalytic degradation of trimethoprim by synthesized S-TiO$_2$ and Ru/WO$_3$/ZrO$_2$ catalysts was investigated. Both photocatalysts have been immobilized on

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circular aluminum plates by polysiloxane to investigate their reusability performance. The

morphology and structure of the catalysts were studied by high-resolution transmission

electron microscopy, X-ray diffraction, and energy-dispersive X-ray spectroscopy. The

photocatalytic experiments were carried out using suspended and attached catalysts using

a metal halide lamp as a light source. The degradation efficiencies of trimethoprim were

100% and 98.2% at catalyst dose of 0.5 g/L, pH of 7.0 and irradiation time of 240 min using

suspended $Ru/WO_3/ZrO_2$ and $S-TiO_2$, respectively. After immobilization of the catalysts

on the aluminum plates, the removal efficiencies in five repetitive cycles were 98%, 96.9%,

96.8%, 93.2% and 83.4% using $Ru/WO_3/ZrO_2$, while they were 88.6%, 86%, 84%, 78%

and 75.9% in case of $S-TiO_2$. The irradiation time of each cycle was 240 min, and the initial

trimethoprim concentration was 10 mg/L. The degradation rates of trimethoprim were

estimated in the case of suspended and immobilized $S-TiO_2$ and $Ru/WO_3/ZrO_2$. The radical

trapping experiments using various scavengers revealed that superoxide radicals, holes and

hydroxyl radicals all participated in the photo-degradation process. Furthermore, the

transformation products generated during the trimethoprim oxidation process were detected

by liquid chromatography/mass spectroscopy to identify the possible degradation pathways.

Keywords:

Pharmaceuticals; Photocatalysis; Transformation products; Trimethoprim; Wastewater

1. Introduction

Antibiotics are frequently released to the aquatic environment through the industrial and domestic

wastewater of pharmaceutical companies as well as the feces of humans and animals [1]. The

immunizing of bacteria against antibiotics due to the prevalence of pharmaceuticals in the aquatic

environment is considered one of the major concerns; therefore, it is essential to develop eco-friendly

methods for the degradation of antibiotics [2]. Trimethoprim is one of the widely used antibiotics

due to its activity towards many types of bacteria; consequently, it has been frequently found in wastewater [3]. Traditional biological wastewater treatment technologies cannot completely remove the bio-resistant contaminants such as antibiotics [4]. Advanced oxidation processes (AOPs) can effectively degrade bio-recalcitrant contaminants through the production of highly active species capable of oxidizing bio-resistant pollutants to harmless products [5].

Photocatalysis is considered one of the promising advanced oxidation processes due to its sustainable nature including low energy consumption and the potential to utilize solar light [6]. Surface recombination is considered one of the major problems associated with conventional semiconductors [7]. Therefore, the doping of various materials on the surface of semiconductors has been investigated. Indeed, the doping can reduce the recombination rate and also participate in the reduction of bandgap [8]. The decrease in the bandgap will enhance the photocatalytic activity towards visible light.

Recently, many studies have added various dopants to conventional catalysts to improve its performance. Chen et al. used the co-hydrolysis method to synthesize cationic S-doped TiO_2 for the oxidation of nitrobenzene, p chlorophenol and phenol in aqueous solutions using a variety of illumination sources [9]. Zeng et al. prepared $WO_3@MoS_2/Ag$ hollow nanotubes using a hydrothermal and deposition method for the degradation of peroxymonosulfate (PMS) [10]. Nano-scale photocatalysts are frequently used in suspension to exploit the high surface area of the particles [11]. However, the dispersion of photocatalysts in water is associated with many limitations such as the difficulty of light penetration due to the high turbidity and the complexity of powder collection for reuse [12]. Therefore, heat attachment methods were successfully used for the loading of catalysts on different mediums; however, they consume high energy in preparation [13]. Moreover, particles can be easily released by the shear force induced by mixing [14].

In this work, the polysiloxane was used to attain durable bonds between photocatalysts and aluminum plates for degradation of trimethoprim. The performance of suspended and attached S-

TiO$_2$ and Ru/WO$_3$/ZrO$_2$ catalysts was investigated. The reusability performance of attached catalysts, oxidant species responsible for photo-degradation, and oxidation pathway were also investigated.

2. Materials and methods

2.1 Materials

Trimethoprim was obtained from MP Bio, USA. Acetonitrile and formic acid were obtained from Sigma-Aldrich. Titanium isopropoxide, ethanol, and ZrO$_2$ were obtained from Wako, Japan. Thiourea was obtained from Tokyo Chemical Industry Co., Ltd. All chemicals were of analytical grade and have been used without any pre-treatments.

2.2 Experimental procedures

The S-TiO$_2$ and Ru/WO$_3$/ZrO$_2$ catalysts were synthesized according to our previous reports (Gar Alalm, Samy, et al., 2018; Gar Alalm, Ookawara, et al., 2016). The attached catalysts were prepared by the immobilization of S-TiO$_2$ and Ru/WO$_3$/ZrO$_2$ particles on aluminum plates using polysiloxane. The diameter and the thickness of aluminum plates are 65 mm and 2 mm, respectively and the aluminum grade is 3003. A strong bond between the catalyst and the aluminum plates can be attained by placing a layer of polysiloxane with a thickness of 1 mm on the surface of the aluminum plate. Then, a uniform distribution of 1 gm of S-TiO$_2$ or Ru/WO$_3$/ZrO$_2$ catalysts was carried out on the aluminum plate with a polysiloxane layer. The drying process of the plates was carried out by keeping the plates at room temperature for 24 hr. The plates were washed by distilled water to remove free particles and confirm the strong bond between the catalyst particles and aluminum plates.

The photo-reactor was about 250 ml Pyrex beaker filled with 100 ml of trimethoprim solution and the light source was maintained at 200 mm from the surface of the solution. The illumination source was a 400 W metal halide lamp (Venture). Metal halide lamps emit visibly and UV light according

The lamp has a maximum

wavelength of 510 nm and 220 μW cm^{-2} is the photon flux of the lamp. The first 30 min in the

experiment were in dark to achieve adsorption-desorption equilibrium, then the lamp was switched

on to start the photo-degradation reaction. The aluminum plate was placed at the bottom of the

beaker and magnetic stirrer was used to achieve a continuous link between the contaminated solution

and the catalyst particles immobilized on the plate. In the case of suspended catalyst, certain doses

of S-TiO$_2$ or Ru/WO$_3$/ZrO$_2$ catalysts were added to the contaminated solution instead of placing the

plate at the bottom of the beaker.

2.3 Analytical methods

Trimethoprim concentrations were detected using HPLC system (Agilent 1200 series, USA).

Filtration of the samples was carried out by Whatman syringe filters (with a pore size of 0.2 μm)

before injection of 20 μL of the sample into a column Apollo C18 (5 mm, 4.6 ×150 mm) and the

column temperature was fixed at 40 °C. The initial mobile phase consists of 30% acetonitrile (A)

and 70% water with 0.1% (V:V) formic acid (B). Then, the percentage of solvent A increased

gradually to 90% within 4 min and this percentage lasted for 2 min. Finally, the percentages of

mobile phase returned to the initial conditions. Trimethoprim peak was observed at a wavelength of

237 nm and the flow rate was 1.5 ml/min [1]. The retention time of the trimethoprim peak was 1.927

min. Identification of transformation products was carried out using liquid chromatography/mass

spectroscopy (LC-MS/MS) (Shimadzu 2020) with a Shim-pack XR-ODS column at a flow rate of

0.4 ml/min using the same mobile phase in HPLC analysis. Transmission electron microscopy (TEM,

Joel JEM 2100, Japan) with an accelerating voltage of 200 kV was used to obtain the images with

high resolution of S-TiO$_2$ and Ru/WO$_3$/ZrO$_2$. The X-ray diffraction (XRD 6000, Shimadzu, Japan)

analysis was used to determine the phases of the crystallinity of S-TiO$_2$ and Ru/WO$_3$/ZrO$_2$ using

122 Cu–Kα radiation (λ=1.54056 Å). The chemical composition of synthesized catalysts was determined

123 using energy dispersive X-ray (EDX) spectroscopy (JEOL JSM-6510LV, Japan).

124

125 **3. Results and discussion**

126 **3.1 Characterization of S-TiO$_2$ and Ru/WO$_3$/ZrO$_2$**

127 The TEM images (Fig. 1 (a)) showed that the diameter of S-TiO$_2$ particles ranged from 12 to 22 nm,

128 while the Ru/WO$_3$/ZrO$_2$ particle diameter ranged from 12 to 27 nm as demonstrated in Fig. 1b. The

129 small diameters of both S-TiO$_2$ and Ru/WO$_3$/ZrO$_2$ particles suggest the high catalytic surface area

130 of the photocatalysts. EDX analysis (Fig. 2) confirmed the presence of Ru, W, and Zr in the prepared

131 Ru/WO$_3$/ZrO$_2$ and the existence of sulfur and titanium in the synthesized S-TiO$_2$ was also confirmed

132 using EDX analysis according to our previous study [8]. Fig. 3 shows the XRD pattern of the

133 synthesized S-TiO$_2$ and Ru/WO$_3$/ZrO$_2$ catalysts. The highest peak was detected at 2θ =25.5^o for S-

134 TiO$_2$ catalyst which belongs to active anatase TiO$_2$ [17]. The peaks at 2θ= 37.6°, 48.1°, 54.20°, 55.4°,

135 and 62.5° are attributed to the various planes of anatase phase of TiO$_2$ (JCPDS no. 21-1272) [18].

136 The existence of a small peak at 2θ= 30.5^o may be due to the remaining amounts of the brookite

137 phase of titania [18]. The sulfur has no unique peaks due to the uniform dispersion of its ions with

138 anatase crystallite [19]. The monoclinic phase of the WO$_3$ crystals was detected through the three

139 peaks observed at $2\theta \approx$ 23–24.3^o (PDF No. 83-0951) as shown in Fig. 3. The existence of free

140 tungstate anions on the catalyst surface was confirmed by the peaks at $2\theta \approx$ 22.9^o, 23.7^o, and 24.4^o

141 [20]. The peaks at 2θ = 28.9^o, 33.8^o, and 34.5^o are due to the tetragonal crystal phase of ZrO$_2$ (PDF

142 number, 27-0997). The peaks of the tetragonal crystal phase were broader due to the addition of Ru

143 (PDF number, 00-006-0663) [15].

144

145

146 **3.2 The photocatalytic activity of the suspended catalyst**

Preliminary studies were performed to check the effect of pH on the degradation of trimethoprim using S-TiO$_2$ and Ru/WO$_3$/ZrO$_2$ at a catalyst dose of 0.5 g/L and a reaction time of 240 min. Fig. S2 demonstrates that the change in pH had a slight effect on the degradation of trimethoprim using both photocatalysts. Hence, the followed experiments were performed without pH adjustment.

The effects of doses of suspended S-TiO$_2$ and Ru/WO$_3$/ZrO$_2$ catalysts on the removal efficiency of trimethoprim are shown in Fig.4. The five levels of S-TiO$_2$ dose (0.1 g/L-1.0 g/L) were used at initial trimethoprim concentration of 10 mg/L, pH of 7, and irradiation time of 240 min, whereas the three levels (0.25 g/L-1.0 g/L) of Ru/WO$_3$/ZrO$_2$ dose were studied at the same conditions. The removal efficiencies due to adsorption during the 30 min incubation in the dark were 6.0%, 9.90%, 2.0%, 3.40% and 12.40% using 0.1 g/L, 0.25 g/L, 0.5 g/L, 0.8 g/L and 1.0 g/L doses of S-TiO$_2$, respectively, while the degradation efficiencies in the dark were 7.0%, 32.0% and 23.50% using 0.25 g/L, 0.5 g/L and 1.0 g/L doses of Ru/WO$_3$/ZrO$_2$, respectively confirming that the overall removal efficiency was mainly due to the photocatalytic degradation. The photo-degradation efficiency increased from 79.3% to 98.2% by increasing the catalyst dose of S-TiO$_2$ from 0.1 g/L to 0.5 g/L. The degradation efficiency was also increased from 94.6% to 100% using Ru/WO$_3$/ZrO$_2$ catalyst dose of 0.25 g/L and 0.5 g/L, respectively after 240 min. Moreover, the complete degradation of trimethoprim was achieved at an irradiation time of 180 min using 1.0 g/L of Ru/WO$_3$/ZrO$_2$. The rise in catalyst dose leads to the enhancement of photo-degradation efficiency possibly due to the increase of active sites responsible for the generation of hydroxyl radicals [8]. Raising S-TiO$_2$ loading to greater than 0.5 g/L, however, led to a slight reduction of photo-degradation efficiency to 95.6% and 94% at catalyst dose of 0.8 g/L and 1.0 g/L, respectively. It may be explained by the fact that higher doses of the catalyst lead to an increase of the turbidity of the solution, hindering photons to reach the active sites of the catalyst surface due to the scattering effect [21]. Furthermore, the possibility of agglomeration of particles can be increased in the case of higher doses and this can lead to the reduction of active

171 sites [22]. Accordingly, the optimum catalyst dose is considered 0.5 g/L in the case of the S-TiO$_2$

172 catalyst.

173

174 **3.3 Photocatalytic activity and reusability of the attached catalyst**

175 The reusability of the attached S-TiO$_2$ and Ru/WO$_3$/ZrO$_2$ catalysts was investigated in five

176 consecutive experiments at initial trimethoprim concentration of 10 mg/L, pH of 7.0 and time of 240

177 min as depicted in Fig. 5 a and b. Ru/WO$_3$/ZrO$_2$ showed higher performance and reusability potential

178 than S-TiO$_2$ in five consecutive cycles. The degradation efficiencies were 98%, 96.9%, 96.8%,

179 93.2% and 83.4% using attached Ru/WO$_3$/ZrO$_2$ in the five repetitive cycles, while the removal

180 efficiencies were 88.6%, 86%, 84%, 78% and 75.9% in case of S-TiO$_2$. The high performance of

181 Ru/WO$_3$/ZrO$_2$ can be attributed to the existence of Ru and Zr ions which act as an electron trap and

182 inhibit the recombination of radicals. The observed degradation efficiency in five consecutive

183 experiments confirmed the high stability and reusability of both S-TiO$_2$ and Ru/WO$_3$/ZrO$_2$ catalysts.

184 The continuous generation of hydroxyl radicals during five consecutive cycles suggest the

185 availability of active sites on the aluminum plate even after a long period of irradiation. The slight

186 decrease in photo-degradation efficiency in each successive cycle may be related to the small amount

187 of catalyst released from the plate and/or leftovers of contaminants on the catalyst decreasing the

188 active surface area.

189 In general, the performance of the attached catalyst is lower than the suspended catalyst at the same

190 condition most likely because the interaction between pollutants and the catalyst only takes place at

191 the bottom of the reactor. Additionally, the light needs to pass through the total depth of the water

192 to excite the catalyst particles. The shear and friction forces resulting from the rapid movement of

193 the stirrer at the bottom of the reactor can result in the release of catalyst particles from the plate.

194 However, the results showed that attached S-TiO$_2$ and Ru/WO$_3$/ZrO$_2$ by polysiloxane have the

195 potential for reusability several times. Moreover, the attached catalyst is more sustainable than

196 suspended catalysts due to the difficulty of collecting suspended catalyst especially nano-scale

197 catalysts. Increasing the illumination time can overcome the limitations related to the attached

198 catalyst and contribute to the reduction of the cost in the case of large-scale application.

199

200 **3.4 Degradation Kinetics of trimethoprim**

201 Langmuir – Hinshelwood model was used to estimate the degradation rates of trimethoprim using

202 S-TiO$_2$ and Ru/WO$_3$/ZrO$_2$ in suspended and attached modes. Eq.1 illustrates the relation between

203 the remaining concentration of trimethoprim and time [23]:

204 $$\ln(\frac{C_O}{C}) = K_{obs}\, t \tag{1}$$

205 where K_{obs} is the reaction rate, C_o and C are the initial concentration of trimethoprim and the

206 concentration of trimethoprim at time t.

207 The degradation rates of trimethoprim using Ru/WO$_3$/ZrO$_2$ in suspended and immobilized modes

208 were higher than the degradation rates in the case of S-TiO$_2$ in both cases as shown in Fig. 6 (a and

209 b). The superiority of Ru/WO$_3$/ZrO$_2$ catalyst in attached and suspended modes was due to the

210 addition of Zr and Ru ions which have the ability to catch electrons and reduce recombination rate

211 leading to higher photodegradation efficiency. Moreover, the degradation rate in suspended mode

212 was higher than the degradation rate in an immobilized mode in the case of both catalysts. In the

213 case of the attached mode, the light needs to pass the total depth of the water to reach the active sites

214 of the immobilized catalyst and generate reactive species, while the light excites the catalyst particles

215 everywhere in the solution using suspended catalysts. Furthermore, the contact between the catalyst

216 particles and the pollutant is higher in the case of suspended catalysts, as the contact only takes place

217 at the bottom of the reactor using attached catalysts. Table 1 shows the degradation rates of

218 trimethoprim using S-TiO$_2$ and Ru/WO$_3$/ZrO$_2$ suspended and immobilized catalysts.

219

Table 1 Degradation rates of trimethoprim in case of suspended and immobilized S-TiO$_2$ and Ru/WO$_3$/ZrO$_2$ catalysts.

Catalyst type	S-TiO$_2$		Ru/WO$_3$/ZrO$_2$	
	R^2	K$_{obs}$	R^2	K$_{obs}$
Suspended mode	0.9082	0.01	0.9709	0.0191
Immobilized mode	0.8898	0.0072	.9573	0.0168

3.5 Degradation mechanism

Fig. 7 demonstrates the generated radicals for the degradation of trimethoprim. The excitation of S-TiO$_2$ and Ru/WO$_3$/ZrO$_2$ by the 400 W metal halide lamp leads to the migration of electrons from the valence band (VB) to the conduction band (CB) leaving holes in the valence band. The reaction of electrons in CB with oxygen (O$_2$) results in the formation of superoxide radicals ($^-$O$_2^-$), while holes (VB) react with water or hydroxyl ions (OH$^-$) to generate hydroxyl radicals ($^.$OH). Holes, hydroxyl radicals and superoxide radicals are in charge of the degradation of trimethoprim. Isopropanol (ISO), ammonium oxalate (AO) and ascorbic acid (AA) were used as scavengers for hydroxyl radicals, superoxide radicals, and holes, respectively to specify the active species responsible for the degradation of trimethoprim as shown in Fig. 8 [24–26]. The degradation efficiency of trimethoprim (10 mg/L) by S-TiO$_2$ was 98.2% without the addition of any scavengers, while the photo-degradation efficiency decreased to 82.8%, 93.3% and 44.9% using 1 mM of ISO, AO, and AA, respectively at a dose of 0.5 g/L, pH of 7, and irradiation time of 240 min as illustrated in Fig. 8 (a). In the case of Ru/WO$_3$/ZrO$_2$, the photo-degradation efficiency reduced to 85%, 92.9% and 48% using 1 mM of ISO, AO, and AA, respectively at the same previous conditions. The results confirmed that hydroxyl radicals, holes, and superoxide radicals all contributed to the degradation

240 process; however, the holes contributed to a greater extent than superoxide radicals and hydroxyl

241 radicals.

242

243 **3.6 Photo-degradation transformation products and potential degradation pathway**

244 The transformation products generated during the photo-degradation process of trimethoprim (TMP;

245 $C_{14}H_{19}N_4O_3$; m/z 291) were measured by mass spectrometry as shown in Fig. 9. Hydroxylation, de-

246 methylation, and cleavage are the main reactions in the TMP degradation process by radicals as

247 reported in the literature [27]. Compounds with the general formula of $C_{14}H_{19}N_4O_{3+x}$ (x varying from

248 1 to 4) can be formed through hydroxylation reaction. These compounds can be classified into mono,

249 bi, tetra- and penta-hydroxylated compounds depending on the value of x. The mono- hydroxylated

250 intermediate (m/z 307; $C_{14}H_{19}N_4O_4$) was identified as α-hydro-xytrimethoprim (TMP–OH) and

251 formed through the hydroxylation of trimethoprim [27]. Di-hydroxylated (m/z 323; $C_{14}H_{19}N_4O_5$)

252 was also formed through the hydroxylation of trimethoprim [28]. The products (α-ketotrimethoprim,

253 TMP=O, m/z 305) can be generated through the oxidation of TMP. Products with formula $C_{14-y}H_{19-2y}N_4O_{3+x}$

254 $_{2y}N_4O_{3+x}$ (y varying from 1 to 3) can be generated through de-methylation reactions. Compounds

255 with (m/z 309; $C_{13}H_{17}N_4O_5$, m/z 341; $C_{13}H_{17}N_4O_7$, m/z 295; $C_{12}H_{15}N_4O_5$, m/z 279; $C_{12}H_{15}N_4O_4$, m/z

256 281; $C_{11}H_{13}N_4O_5$ and m/z 277; $C_{13}H_{16}N_4O_3$) were formed through de-methylation/hydroxylation

257 process of TMP [28]. Products (m/z= 139; $C_5H_6N_4O$, m/z 155; $C_5H_6N_4O_2$, m/z 171; $C_8H_{10}O_4$ and

258 m/z 141; $C_5H_8N_4O$) were suggested to be generated by the cleavage of TMP [28]. Based on the

259 observation of these transformation products, a possible degradation pathway is suggested in Fig. 9.

260

261 **4. Conclusions**

262 S-TiO$_2$ and Ru/WO$_3$/ZrO$_2$ catalysts were synthesized and their performance in the attached and

263 suspended state was evaluated for the degradation of trimethoprim. The characterization of the

264 synthesized S-TiO$_2$ and Ru/WO$_3$/ZrO$_2$ catalysts suggested a successful interaction of components

and high active surface area. The optimum catalyst doses in suspension state of S-TiO$_2$, and Ru/WO$_3$/ZrO$_2$ were 0.5 and 1.0 g/L, respectively. The degradation efficiencies of trimethoprim were 100% and 98.2% at catalyst dose of 0.5 g/L, pH of 7.0 and irradiation time of 240 min using suspended Ru/WO$_3$/ZrO$_2$ and S-TiO$_2$, respectively. Ru/WO$_3$/ZrO$_2$ showed higher performance and reusability than S-TiO$_2$ in five consecutive runs in the attached state. The removal efficiencies in five consecutive runs were 88.6%, 86%, 84%, 78% and 75.9% for the attached S-TiO$_2$, while the degradation rates were 98%, 96.9%, 96.8%, 93.2% and 83.4% in case of attached Ru/WO$_3$/ZrO$_2$. The degradation rates of trimethoprim in the case of the immobilized mode were lower than the degradation rates using catalysts in suspended mode. The main active species in charge of the photo-degradation process were holes and hydroxyl radicals. The potential degradation pathways were suggested based on the identification of transformation products.

Acknowledgment

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