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著者	Samy Mahmoud, Ibrahim Mona G., Gar Alalm Mohamed, Fujii Manabu, Ookawara Shinichi, Ohno Teruhisa
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Photocatalytic degradation of Trimethoprim using S-TiO₂ and Ru/WO₃/ZrO₂ immobilized on reusable fixed plates

Mahmoud Samy^{a, *}, Mona G. Ibrahim^{a,b}, Mohamed Gar Alalm^{c, †}, Manabu Fujii^{a,d}, Shinichi Ookawara^{e,f}, Teruhisa Ohno^g

^a *Environmental Engineering Department, Egypt-Japan University of Science and Technology (E-Just), New Borg El Arab City, Alexandria 21934, Egypt*

^b *Environmental Health Department, High Institute of Public Health, Alexandria University, Alexandria 21544, Egypt*

^c *Department of Public Works Engineering, Faculty of Engineering, Mansoura University, Mansoura 35516, Egypt*

^d *Department of Civil and Environmental Engineering, Tokyo Institute of Technology, Meguro-ku, Tokyo 152-8552, Japan*

^e *Department of Chemical Science and Engineering, Tokyo Institute of Technology, Tokyo 152-8552, Japan*

^f *Dept. of Energy Resources Engineering, Egypt-Japan University of Science and Technology, Alexandria 21934, Egypt*

^g *Department of Applied Chemistry, Faculty of Engineering, Kyushu Institute of Technology, 1-1 Sensuicho, Tobata, Kitakyushu 804-8550, Japan*

Abstract

In this study, photocatalytic degradation of trimethoprim by synthesized S-TiO₂ and Ru/WO₃/ZrO₂ catalysts was investigated. Both photocatalysts have been immobilized on

* Corresponding authors:

Tel: +20 10 18262849, E-mail address: mahmoud.samy@ejust.edu.eg

† Tel: +20 12 89488300, E-mail address: m_gar_alalm@mans.edu.eg

23 circular aluminum plates by polysiloxane to investigate their reusability performance. The
24 morphology and structure of the catalysts were studied by high-resolution transmission
25 electron microscopy, X-ray diffraction, and energy-dispersive X-ray spectroscopy. The
26 photocatalytic experiments were carried out using suspended and attached catalysts using
27 a metal halide lamp as a light source. The degradation efficiencies of trimethoprim were
28 100% and 98.2% at catalyst dose of 0.5 g/L, pH of 7.0 and irradiation time of 240 min using
29 suspended Ru/WO₃/ZrO₂ and S-TiO₂, respectively. After immobilization of the catalysts
30 on the aluminum plates, the removal efficiencies in five repetitive cycles were 98%, 96.9%,
31 96.8%, 93.2% and 83.4% using Ru/WO₃/ZrO₂, while they were 88.6%, 86%, 84%, 78%
32 and 75.9% in case of S-TiO₂. The irradiation time of each cycle was 240 min, and the initial
33 trimethoprim concentration was 10 mg/L. The degradation rates of trimethoprim were
34 estimated in the case of suspended and immobilized S-TiO₂ and Ru/WO₃/ZrO₂. The radical
35 trapping experiments using various scavengers revealed that superoxide radicals, holes and
36 hydroxyl radicals all participated in the photo-degradation process. Furthermore, the
37 transformation products generated during the trimethoprim oxidation process were detected
38 by liquid chromatography/mass spectroscopy to identify the possible degradation pathways.

39 **Keywords:**

40 Pharmaceuticals; Photocatalysis; Transformation products; Trimethoprim; Wastewater

41

42 **1. Introduction**

43 Antibiotics are frequently released to the aquatic environment through the industrial and domestic
44 wastewater of pharmaceutical companies as well as the feces of humans and animals [1]. The
45 immunizing of bacteria against antibiotics due to the prevalence of pharmaceuticals in the aquatic
46 environment is considered one of the major concerns; therefore, it is essential to develop eco-friendly
47 methods for the degradation of antibiotics [2]. Trimethoprim is one of the widely used antibiotics

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

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

60 Recently, many studies have added various dopants to conventional catalysts to improve its
61 performance. Chen et al. used the co-hydrolysis method to synthesize cationic S-doped TiO₂ for the
62 oxidation of nitrobenzene, p chlorophenol and phenol in aqueous solutions using a variety of
63 illumination sources [9]. Zeng et al. prepared WO₃@MoS₂/Ag hollow nanotubes using a
64 hydrothermal and deposition method for the degradation of peroxydisulfate (PDS) [10]. Nano-
65 scale photocatalysts are frequently used in suspension to exploit the high surface area of the particles
66 [11]. However, the dispersion of photocatalysts in water is associated with many limitations such as
67 the difficulty of light penetration due to the high turbidity and the complexity of powder collection
68 for reuse [12]. Therefore, heat attachment methods were successfully used for the loading of
69 catalysts on different mediums; however, they consume high energy in preparation [13]. Moreover,
70 particles can be easily released by the shear force induced by mixing [14].

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

73 TiO₂ and Ru/WO₃/ZrO₂ catalysts was investigated. The reusability performance of attached catalysts,
74 oxidant species responsible for photo-degradation, and oxidation pathway were also investigated.

75

76 **2. Materials and methods**

77 **2.1 Materials**

78 Trimethoprim was obtained from MP Bio, USA. Acetonitrile and formic acid were obtained from
79 Sigma-Aldrich. Titanium isopropoxide, ethanol, and ZrO₂ were obtained from Wako, Japan.
80 Thiourea was obtained from Tokyo Chemical Industry Co., Ltd. All chemicals were of analytical
81 grade and have been used without any pre-treatments.

82

83 **2.2 Experimental procedures**

84 The S-TiO₂ and Ru/WO₃/ZrO₂ catalysts were synthesized according to our previous reports (Gar
85 Alalm, Samy, et al., 2018; Gar Alalm, Ookawara, et al., 2016). The attached catalysts were prepared
86 by the immobilization of S-TiO₂ and Ru/WO₃/ZrO₂ particles on aluminum plates using polysiloxane.
87 The diameter and the thickness of aluminum plates are 65 mm and 2 mm, respectively and the
88 aluminum grade is 3003. A strong bond between the catalyst and the aluminum plates can be attained
89 by placing a layer of polysiloxane with a thickness of 1 mm on the surface of the aluminum plate.
90 Then, a uniform distribution of 1 gm of S-TiO₂ or Ru/WO₃/ZrO₂ catalysts was carried out on the
91 aluminum plate with a polysiloxane layer. The drying process of the plates was carried out by
92 keeping the plates at room temperature for 24 hr. The plates were washed by distilled water to
93 remove free particles and confirm the strong bond between the catalyst particles and aluminum
94 plates.

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

98 to the emission profile of metal halide lamps as shown in Fig. S1 [16]. The lamp has a maximum
99 wavelength of 510 nm and $220 \mu\text{W cm}^{-2}$ is the photon flux of the lamp. The first 30 min in the
100 experiment were in dark to achieve adsorption-desorption equilibrium, then the lamp was switched
101 on to start the photo-degradation reaction. The aluminum plate was placed at the bottom of the
102 beaker and magnetic stirrer was used to achieve a continuous link between the contaminated solution
103 and the catalyst particles immobilized on the plate. In the case of suspended catalyst, certain doses
104 of S-TiO₂ or Ru/WO₃/ZrO₂ catalysts were added to the contaminated solution instead of placing the
105 plate at the bottom of the beaker.

106

107 **2.3 Analytical methods**

108 Trimethoprim concentrations were detected using HPLC system (Agilent 1200 series, USA).
109 Filtration of the samples was carried out by Whatman syringe filters (with a pore size of 0.2 μm)
110 before injection of 20 μL of the sample into a column Apollo C18 (5 mm, 4.6 \times 150 mm) and the
111 column temperature was fixed at 40 °C. The initial mobile phase consists of 30% acetonitrile (A)
112 and 70% water with 0.1% (V:V) formic acid (B). Then, the percentage of solvent A increased
113 gradually to 90% within 4 min and this percentage lasted for 2 min. Finally, the percentages of
114 mobile phase returned to the initial conditions. Trimethoprim peak was observed at a wavelength of
115 237 nm and the flow rate was 1.5 ml/min [1]. The retention time of the trimethoprim peak was 1.927
116 min. Identification of transformation products was carried out using liquid chromatography/mass
117 spectroscopy (LC-MS/MS) (Shimadzu 2020) with a Shim-pack XR-ODS column at a flow rate of
118 0.4 ml/min using the same mobile phase in HPLC analysis. Transmission electron microscopy (TEM,
119 Joel JEM 2100, Japan) with an accelerating voltage of 200 kV was used to obtain the images with
120 high resolution of S-TiO₂ and Ru/WO₃/ZrO₂. The X-ray diffraction (XRD 6000, Shimadzu, Japan)
121 analysis was used to determine the phases of the crystallinity of S-TiO₂ and Ru/WO₃/ZrO₂ using

122 Cu-K α radiation ($\lambda=1.54056 \text{ \AA}$). 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-TiO₂ and Ru/WO₃/ZrO₂**

127 The TEM images (Fig. 1 (a)) showed that the diameter of S-TiO₂ particles ranged from 12 to 22 nm,
128 while the Ru/WO₃/ZrO₂ particle diameter ranged from 12 to 27 nm as demonstrated in Fig. 1b. The
129 small diameters of both S-TiO₂ and Ru/WO₃/ZrO₂ 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/WO₃/ZrO₂ and the existence of sulfur and titanium in the synthesized S-TiO₂ was also confirmed
132 using EDX analysis according to our previous study [8]. Fig. 3 shows the XRD pattern of the
133 synthesized S-TiO₂ and Ru/WO₃/ZrO₂ catalysts. The highest peak was detected at $2\theta = 25.5^\circ$ for S-
134 TiO₂ catalyst which belongs to active anatase TiO₂ [17]. The peaks at $2\theta = 37.6^\circ, 48.1^\circ, 54.20^\circ, 55.4^\circ,$
135 and 62.5° are attributed to the various planes of anatase phase of TiO₂ (JCPDS no. 21-1272) [18].
136 The existence of a small peak at $2\theta = 30.5^\circ$ 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 WO₃ crystals was detected through the three
139 peaks observed at $2\theta \approx 23\text{--}24.3^\circ$ (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 $2\theta \approx 22.9^\circ, 23.7^\circ,$ and 24.4°
141 [20]. The peaks at $2\theta = 28.9^\circ, 33.8^\circ,$ and 34.5° are due to the tetragonal crystal phase of ZrO₂ (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**

147 Preliminary studies were performed to check the effect of pH on the degradation of trimethoprim
148 using S-TiO₂ and Ru/WO₃/ZrO₂ at a catalyst dose of 0.5 g/L and a reaction time of 240 min. Fig. S2
149 demonstrates that the change in pH had a slight effect on the degradation of trimethoprim using both
150 photocatalysts. Hence, the followed experiments were performed without pH adjustment.

151 The effects of doses of suspended S-TiO₂ and Ru/WO₃/ZrO₂ catalysts on the removal efficiency of
152 trimethoprim are shown in Fig.4. The five levels of S-TiO₂ dose (0.1 g/L-1.0 g/L) were used at initial
153 trimethoprim concentration of 10 mg/L, pH of 7, and irradiation time of 240 min, whereas the three
154 levels (0.25 g/L-1.0 g/L) of Ru/WO₃/ZrO₂ dose were studied at the same conditions. The removal
155 efficiencies due to adsorption during the 30 min incubation in the dark were 6.0%, 9.90%, 2.0%,
156 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-TiO₂, respectively,
157 while the degradation efficiencies in the dark were 7.0%, 32.0% and 23.50% using 0.25 g/L, 0.5 g/L
158 and 1.0 g/L doses of Ru/WO₃/ZrO₂, respectively confirming that the overall removal efficiency was
159 mainly due to the photocatalytic degradation. The photo-degradation efficiency increased from
160 79.3% to 98.2% by increasing the catalyst dose of S-TiO₂ from 0.1 g/L to 0.5 g/L. The degradation
161 efficiency was also increased from 94.6% to 100% using Ru/WO₃/ZrO₂ catalyst dose of 0.25 g/L
162 and 0.5 g/L, respectively after 240 min. Moreover, the complete degradation of trimethoprim was
163 achieved at an irradiation time of 180 min using 1.0 g/L of Ru/WO₃/ZrO₂. The rise in catalyst dose
164 leads to the enhancement of photo-degradation efficiency possibly due to the increase of active sites
165 responsible for the generation of hydroxyl radicals [8]. Raising S-TiO₂ loading to greater than 0.5
166 g/L, however, led to a slight reduction of photo-degradation efficiency to 95.6% and 94% at catalyst
167 dose of 0.8 g/L and 1.0 g/L, respectively. It may be explained by the fact that higher doses of the
168 catalyst lead to an increase of the turbidity of the solution, hindering photons to reach the active sites
169 of the catalyst surface due to the scattering effect [21]. Furthermore, the possibility of agglomeration
170 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-TiO₂
172 catalyst.

173

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

175 The reusability of the attached S-TiO₂ and Ru/WO₃/ZrO₂ 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/WO₃/ZrO₂ showed higher performance and reusability potential
178 than S-TiO₂ in five consecutive cycles. The degradation efficiencies were 98%, 96.9%, 96.8%,
179 93.2% and 83.4% using attached Ru/WO₃/ZrO₂ in the five repetitive cycles, while the removal
180 efficiencies were 88.6%, 86%, 84%, 78% and 75.9% in case of S-TiO₂. The high performance of
181 Ru/WO₃/ZrO₂ 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-TiO₂ and Ru/WO₃/ZrO₂ 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-TiO₂ and Ru/WO₃/ZrO₂ 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-TiO₂ and Ru/WO₃/ZrO₂ in suspended and attached modes. Eq.1 illustrates the relation between
203 the remaining concentration of trimethoprim and time [23]:

$$204 \quad \ln\left(\frac{C_0}{C}\right) = K_{obs} t \quad (1)$$

205 where K_{obs} is the reaction rate, C_0 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/WO₃/ZrO₂ in suspended and immobilized modes
208 were higher than the degradation rates in the case of S-TiO₂ in both cases as shown in Fig. 6 (a and
209 b). The superiority of Ru/WO₃/ZrO₂ 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-TiO₂ and Ru/WO₃/ZrO₂ suspended and immobilized catalysts.

219

220 **Table 1** Degradation rates of trimethoprim in case of suspended and immobilized S-TiO₂ and
221 Ru/WO₃/ZrO₂ 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

222

223

224 **3.5 Degradation mechanism**

225 Fig. 7 demonstrates the generated radicals for the degradation of trimethoprim. The excitation of S-
226 TiO₂ and Ru/WO₃/ZrO₂ by the 400 W metal halide lamp leads to the migration of electrons from
227 the valence band (VB) to the conduction band (CB) leaving holes in the valence band. The reaction
228 of electrons in CB with oxygen (O₂) results in the formation of superoxide radicals (⁻O₂), while
229 holes (VB) react with water or hydroxyl ions (OH⁻) to generate hydroxyl radicals ([•]OH). Holes,
230 hydroxyl radicals and superoxide radicals are in charge of the degradation of trimethoprim.

231 Isopropanol (ISO), ammonium oxalate (AO) and ascorbic acid (AA) were used as scavengers for
232 hydroxyl radicals, superoxide radicals, and holes, respectively to specify the active species
233 responsible for the degradation of trimethoprim as shown in Fig. 8 [24–26]. The degradation
234 efficiency of trimethoprim (10 mg/L) by S-TiO₂ was 98.2% without the addition of any scavengers,
235 while the photo-degradation efficiency decreased to 82.8%, 93.3% and 44.9% using 1 mM of ISO,
236 AO, and AA, respectively at a dose of 0.5 g/L, pH of 7, and irradiation time of 240 min as illustrated
237 in Fig. 8 (a). In the case of Ru/WO₃/ZrO₂, the photo-degradation efficiency reduced to 85%, 92.9%
238 and 48% using 1 mM of ISO, AO, and AA, respectively at the same previous conditions. The results
239 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 $C_{14-y}H_{19-}$
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; $C_3H_6N_4O$, 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-TiO₂ and Ru/WO₃/ZrO₂ 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-TiO₂ and Ru/WO₃/ZrO₂ catalysts suggested a successful interaction of components

265 and high active surface area. The optimum catalyst doses in suspension state of S-TiO₂, and
266 Ru/WO₃/ZrO₂ were 0.5 and 1.0 g/L, respectively. The degradation efficiencies of trimethoprim were
267 100% and 98.2% at catalyst dose of 0.5 g/L, pH of 7.0 and irradiation time of 240 min using
268 suspended Ru/WO₃/ZrO₂ and S-TiO₂, respectively. Ru/WO₃/ZrO₂ showed higher performance and
269 reusability than S-TiO₂ in five consecutive runs in the attached state. The removal efficiencies in
270 five consecutive runs were 88.6%, 86%, 84%, 78% and 75.9% for the attached S-TiO₂, while the
271 degradation rates were 98%, 96.9%, 96.8%, 93.2% and 83.4% in case of attached Ru/WO₃/ZrO₂.
272 The degradation rates of trimethoprim in the case of the immobilized mode were lower than the
273 degradation rates using catalysts in suspended mode. The main active species in charge of the photo-
274 degradation process were holes and hydroxyl radicals. The potential degradation pathways were
275 suggested based on the identification of transformation products.

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