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1 Acceleration of the photocatalytic degradation of organics by *in-situ* removal of the products
2 of degradation

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11 **Abstract**

12 Photocatalytic degradation of sulphur containing organics in water was substantially
13 accelerated by the *in-situ* removal of sulphur oxide species formed by the dye degradation as
14 metal sulfate precipitates. The significant enhancement of the degradation of methylene blue
15 (C₁₆H₁₈ClN₃S) and acid yellow 42 (C₃₂H₂₄N₈Na₂O₈S₂), as examples of sulphur containing
16 organics, was achieved when the reactions were conducted in the presence of alkaline earth
17 cations (such as Ca²⁺, Sr²⁺, and Ba²⁺).

18 *Keywords: photocatalyst; titania; degradation; equilibrium shift*

19 **1. Introduction**

20 Heterogeneous photocatalysis has been applied for the purification of the contaminated
21 water by the oxidative decomposition of organic substances [1,2] and the concentration of
22 heavy metals (As, Cd, and Cr) [3-8]. Designing structure, composition and morphology of
23 photocatalysts has mainly been examined in order to improve the reaction efficiency [9-16].

24 Alternatively, improved efficiency of photocatalytic reaction has been achieved by adjusting
25 reaction environments and conditions. The effects of pH of solution and the addition of
26 oxidizing agent (H_2O_2) have been investigated for the decomposition of various organic dyes
27 [17,18]. The decomposition of benzene to CO_2 was accelerated by the irradiation under
28 magnetic field [19], and that of an azo dye (acid orange 8) was modified by the irradiation
29 under sonication [20]. The yield and selectivity of the photocatalytic degradation of benzene
30 was affected by the presence of photo-inactive species such as clay minerals [21]. In order to
31 understand the mechanism of those positive effects as well as to improve the reaction efficiency
32 further, new examples on the effects of reaction environment to affect the photocatalytic
33 reactions are worth developing.

34 Here, we propose a new strategy to accelerate the decomposition of organics for
35 wastewater treatment by chemical equilibrium shift, in which a product from the photocatalytic
36 reaction system was removed. The idea in the present study is efficient removal of S oxide
37 species (as sulfates) formed by the decomposition during the irradiation by capturing (*in-situ*
38 removal) the S oxide species as precipitates of alkaline earth sulfates, which have very low
39 solubility in water. Consequently, the dye photodegradation is expected to be promoted due to
40 “equilibrium shift”.

41 Sulphur containing organic compounds were selected as the target organic compounds
42 to be decomposed. The decomposition of sulphur containing azo dyes (e.g. Procion Red,
43 Reactive Brilliant Red, methyl orange) has been investigated in aqueous TiO_2 suspension; the
44 N oxide species as nitrates and S oxide species as sulfates were characterized as the products
45 in the solution after the dye decomposition [22-25]. It was reported that the amount of the
46 sulfate formed in the solution was lower than that expected from stoichiometry [26-32], which
47 indicated that some S oxide species were adsorbed on the surface of the photocatalyst. The
48 adsorption of S oxide species may affect the photocatalytic reaction by blocking the catalyst's

49 surface for the substrate access, so that the capturing of the S oxide species from the reaction
50 system is expected to suppress the deactivation.

51 **2. Experimental methods**

52 *2.1. Materials*

53 TiO_2 (Evonik P25) was purchased from Evonik Industries. Strontium nitrate anhydrous,
54 calcium nitrate tetrahydrate, calcium acetate hydrate, methylene blue, acid yellow 42, and
55 rhodamine 6G were purchased from Sigma-Aldrich Co., Ltd. Barium nitrate and magnesium
56 nitrate hexahydrate were purchased from Alfa Aesar Chemical Co., Ltd. Lithium nitrate was
57 purchased from Honeywell FlukaTM. Sodium chloride and calcium chloride dihydrate was
58 purchased from Merck Ltd. Sodium nitrate solution was prepared by equivalent molar between
59 sodium hydroxide and nitric acid. Sodium hydroxide was purchased from Carlo Erba Reagents
60 S.r.l. Nitric acid was purchased from Chem-Lab NV. All chemicals were used without
61 purification.

62 *2.2. Preparation of photocatalyst film*

63 The photocatalyst film was prepared by casting an aqueous TiO_2 (P25) suspension onto
64 borosilicate glass slides. The suspension was prepared by adding 0.1 g of P25 into 100 ml of
65 DI water with magnetic stirring. Then, 0.8 ml of the P25 suspension was dropped on one side
66 of the borosilicate glass slide and dried at room temperature. The suspension was naturally
67 spread on the glass slide thanks to the wettability of the glass slide after the cleaning with 0.001
68 M of aqueous HCl solution for 1 day. The weight of P25 on the glass slide (ca. around 0.0008
69 g) was confirmed by measuring the weight increase after casting and drying.

70 *2.3. Photocatalytic decomposition experiments*

71 The photocatalytic decomposition of the S containing organic dyes (methylene blue and
72 acid yellow 42) and the organic dye without S (rhodamine 6G) was carried out by putting the

73 film in an aqueous solution of the dyes and irradiated by a UV light (Eurosolar type 795 S
74 Solaria Facial Tanning Sun Face Tanner UV Type 3 as a light source) using four UV lamps
75 Philips CLEO 15 W. The film was immersed into the solution before UV irradiated for 1 h to
76 examine the adsorption of dyes on the TiO₂ surface. To evaluate the role of alkaline earth
77 cations (Ca²⁺, Sr²⁺, and Ba²⁺) on the decomposition of the dyes, the anhydrous strontium nitrate,
78 calcium nitrate tetrahydrate or barium nitrate was added into the dye solutions (initial
79 concentration of the dye at 30 mg/L) as the source of Ca²⁺, Sr²⁺, and Ba²⁺ with fixing
80 concentration of alkaline earth cations at 0.5 M, respectively. The photocatalytic decomposition
81 of the dyes in the presence of sodium chloride, sodium nitrate, and lithium nitrate (as the source
82 of Na⁺ and Li⁺) was further examined to confirm the proposed mechanism under the identical
83 conditions (0.5 M of concentration of the inorganic salts). The effects of co-existing anions on
84 the decomposition of the dyes was examined by adding the 0.5 M of calcium chloride into the
85 solution. The pH of the solution before and after adding alkaline earth cations was measured
86 by pH meter (HANNA, HI2004 edge). The irradiance was 0.01 W/cm², measured at distance
87 between the light source and the photocatalyst film by EIT Power UV Radiometer, 92380
88 GARCHES S/N0491029. The concentration of the dyes after the reaction was directly
89 determined by using JENWAY 7315 Spectrophotometer without any separation processes of
90 powder thanks to advantages of film application and the changes of the concentration of the
91 dyes (the absorbance at 664 nm for methylene blue, at 440 nm for acid yellow 42, and at 530
92 nm for rhodamine 6G) during irradiation were followed.

93 *2.4. Kinetic analyses*

94 Apparent pseudo first-order decomposition rate constant (k) was determined for the
95 evaluation the photocatalytic decomposition of the dyes in the presence and the absence of
96 alkaline earth cations in the solution. The rate constant (k = slope) is derived by the graph

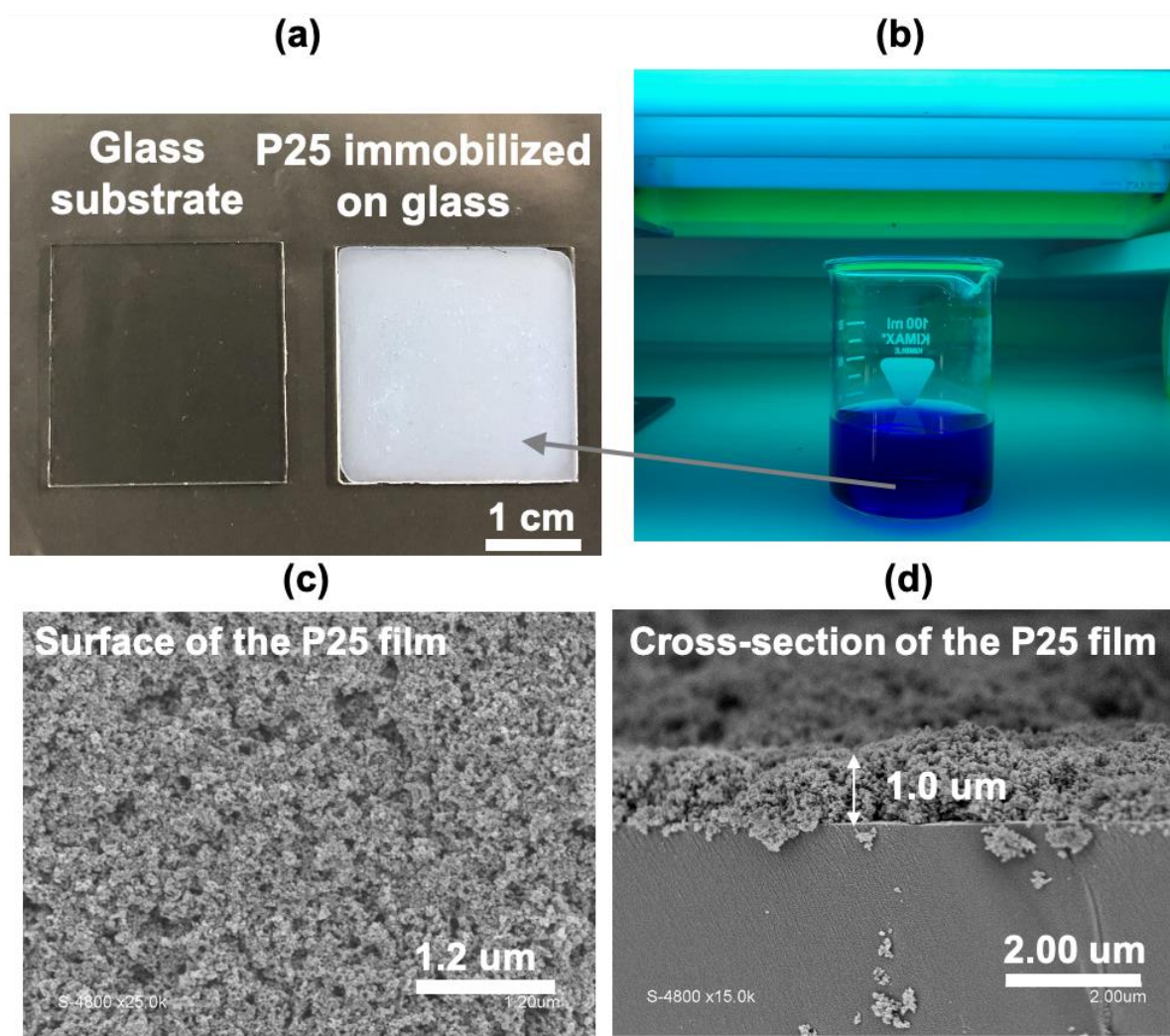
97 relationship between $\ln(C_0/C_t)$ versus irradiation time, where C_0 is initial concentration of the
98 dyes and C_t is concentration of the dyes after the reaction at time t .

99 **3. Results and discussion**

100 *3.1. Morphology and the advantages of the photocatalyst film*

101 In the preliminary experiments using the titania photocatalyst (P25, Evonik, average
102 particle size of 22 nm from Aerosil Co., Ltd.) suspension, the state of the suspension was
103 significantly affected by the presence of metal salts (cause agglomeration and sedimentation,
104 as shown in Fig. S1). In order to avoid the effects of the difference (light scattering, diffusion
105 of reactant etc.) on the photocatalytic reaction, a film of photocatalyst was used in the present
106 study. P25 was employed as the photocatalyst due to its high efficiency for the photocatalytic
107 decomposition of organics and the stability of aqueous suspension. The aqueous suspension
108 was used to prepare homogeneous film on substrate by simple casting [33,34]. The photograph
109 of the P25 film and the SEM images are shown in Fig. 1. The film thickness was around 1.0
110 μm with the estimated porosity of 67% based on the calculation from the volume of solid
111 content (0.0008 g of P25 on the substrate and the density of P25, 3.9 g/cm^3) and the estimated
112 total volume of the film (6.25 cm^2 of the coating area and $1.0 \mu\text{m}$ of the film thickness). The
113 porosity of random close packing of dense spherical particles is $\sim 36\%$ with the assumption for
114 monodispersed particles [35]. The higher porosity of the film (67%) was explained by the
115 sparse aggregation of P25 particles during drying, leading to interconnected pore between the
116 P25 particles as seen in the surface morphology of the film (Fig. 1c). Thanks to the thickness
117 ($1.0 \mu\text{m}$) and the high porosity (67%) of the film, the diffusion of organic molecules inside the
118 particle voids is expected to be easy and all P25 particles in the layer film are photocatalytically
119 active [36]. As the TiO_2 was immobilized on the substrate, alkaline earth sulfate formed after
120 the reaction was expected to be observed by naked eyes as precipitates. Moreover, it was

121 possible to determine the change of the concentration of the organics without the separation of
122 photocatalyst from the reaction mixture.



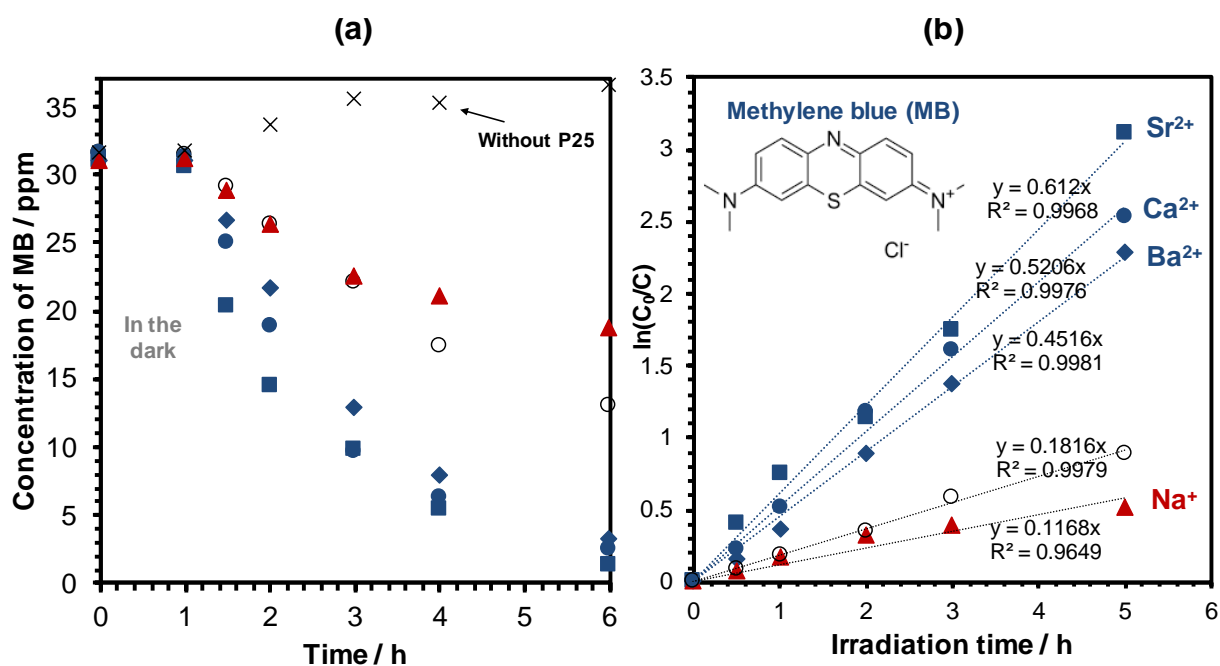
123
124 Fig. 1. (a) Photograph of the P25 immobilized on glass as the film. (b) Experimental set-up by
125 putting the P25 film into the solutions. (c) Surface and (d) cross-section images of the P25 film
126 from SEM observations.

127 3.2. Photocatalytic decomposition of sulphur-containing organics

128 Methylene blue ($C_{16}H_{18}ClN_3S$, abbreviated as MB) was selected as a sulphur containing
129 organic. The photocatalytic decomposition of MB was carried out in the absence or presence
130 of an alkaline cation, Na^+ (adding NaCl), or of alkaline earth cations such as Ca^{2+} , Sr^{2+} , and

131 Ba^{2+} (adding $\text{Ca}(\text{NO}_3)_2$, $\text{Sr}(\text{NO}_3)_2$, and $\text{Ba}(\text{NO}_3)_2$) in the solution, respectively (Fig. 2a). The
132 decomposition of MB was accelerated when the reaction was conducted in the presence of
133 Ca^{2+} , Sr^{2+} , and Ba^{2+} (Fig. 2b). When the reaction was conducted in the presence of Na^+ in the
134 solution, the decomposition rate was not improved and slightly retarded after the UV irradiation
135 for 2 h. The adsorption of MB on the P25 film has here to be discussed considering the surface
136 charge of titania. The pH of solution changed from 6.48 to 6.41, 5.86, 5.91, and 5.64 after the
137 addition of NaCl, $\text{Ca}(\text{NO}_3)_2$, $\text{Sr}(\text{NO}_3)_2$, $\text{Ba}(\text{NO}_3)_2$ in the solution, respectively. The isoelectric
138 point of P25 is reported to be around 6 [37]. Adsorption of MB on the P25 film was not
139 observed for the reaction in $\text{Ca}(\text{NO}_3)_2$, $\text{Sr}(\text{NO}_3)_2$, and $\text{Ba}(\text{NO}_3)_2$ solutions. The adsorption of
140 humic acid on TiO_2 was before claimed as the main reason to promote the decomposition of
141 humic acid in aqueous suspension containing Ca^{2+} [38]. The present phenomena are therefore
142 not explained by the effects of the MB adsorption.

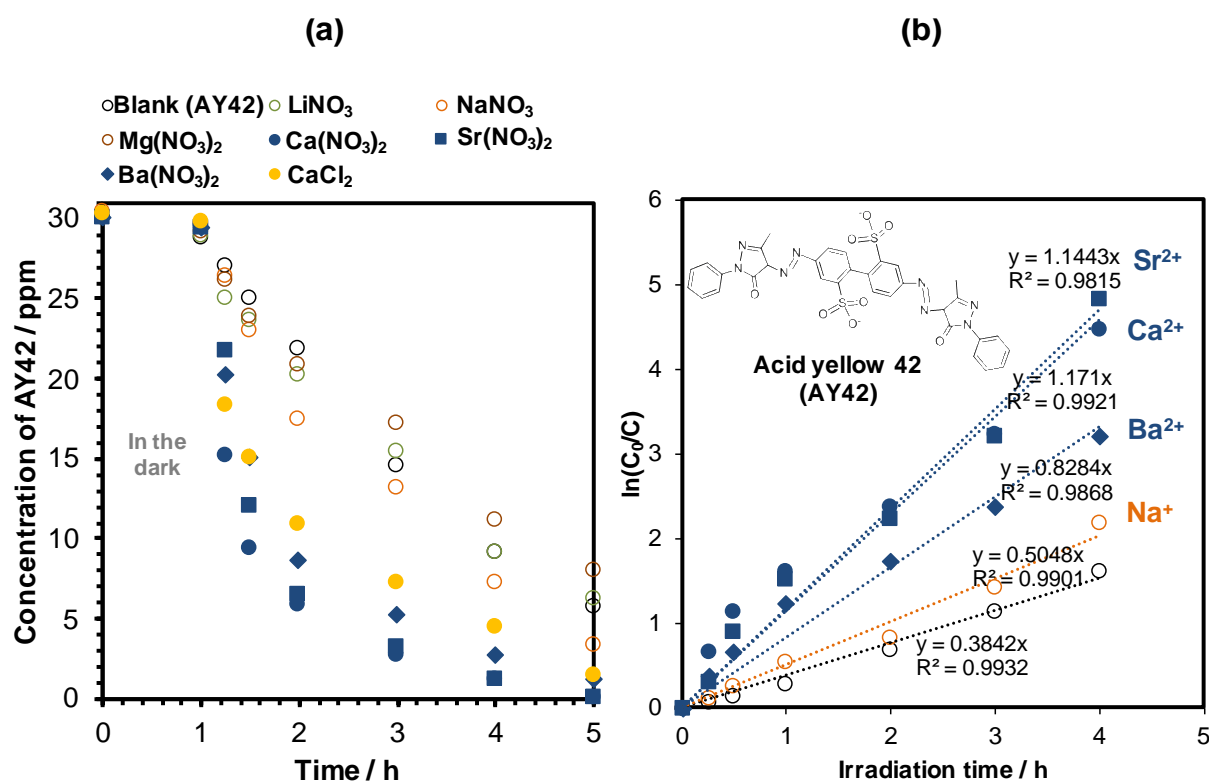
143 The decomposition of MB in the presence of $\text{Mg}(\text{NO}_3)_2$, LiNO_3 and NaNO_3 was also
144 examined. The concentration of MB decreased from 30 ppm to 27 ppm by the addition of
145 $\text{Mg}(\text{NO}_3)_2$, LiNO_3 , and NaNO_3 into the MB solution in the dark, suggesting that the adsorption
146 of MB on P25 by the electrostatic interactions happened to some extent by the change of pH
147 (from 6.48 to 7.32, 9.21, and 12.10 for $\text{Mg}(\text{NO}_3)_2$, LiNO_3 and NaNO_3 systems, respectively).



148
 149 Fig. 2. Photocatalytic decomposition of (a) MB and (b) apparent pseudo first order plot of the
 150 MB decomposition by using the P25 film in the absence (black open circle) and the presence
 151 of Na⁺ (red triangle) and alkaline earth cations (Ca²⁺; blue full circle, Sr²⁺; blue square, and
 152 Ba²⁺; blue diamond) by adding NaCl, Ca(NO₃)₂, Sr(NO₃)₂, and Ba(NO₃)₂ in the solution,
 153 respectively.

154 An anionic dye, acid yellow 42 (C₃₂H₂₄N₈Na₂O₈S₂, abbreviated as AY42), was chosen
 155 as another example of sulphur containing organics to be examined for the photocatalytic
 156 decomposition in the presence of metal salts. The photocatalytic decomposition of AY42 was
 157 successfully accelerated in the presence of Ca²⁺, Sr²⁺ and Ba²⁺, whereas no significant effects
 158 on the decomposition of AY42 were observed by the addition of Mg²⁺, Na⁺ and Li⁺ (Fig. 3a).
 159 The decomposition of AY42 was also accelerated when CaCl₂ was added. Thus, the
 160 decomposition rate of MB and AY42 was accelerated by the presence of Ca²⁺, Sr²⁺ and Ba²⁺,
 161 and was not affected by the co-existing anions (NO₃⁻ or Cl⁻). The rate constants of the
 162 decomposition of AY42 were 0.83, 1.17, and 1.14 h⁻¹ for the reactions in the presence of Ba²⁺,
 163 Ca²⁺, and Sr²⁺, respectively (Fig. 3b). The decomposition of AY42 was faster than that of MB

164 under the present conditions, which is thought to be due to the difference in the decomposition
 165 pathways of AY42 and MB [31].

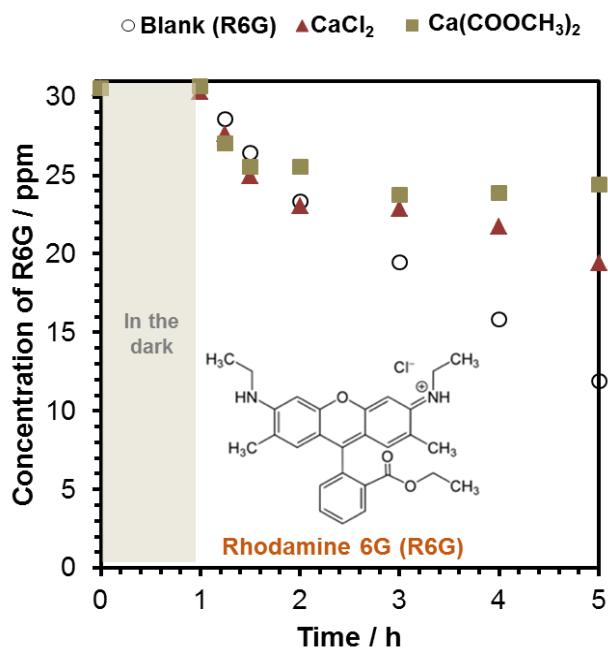


166
 167 Fig. 3. (a) Photocatalytic decomposition of AY42 and (b) apparent pseudo first order plot of
 168 the AY42 decomposition by using the P25 film in the absence and the presence of inorganic
 169 salts such as LiNO₃, NaNO₃, Mg(NO₃)₂, Ca(NO₃)₂, CaCl₂, Sr(NO₃)₂, and Ba(NO₃)₂.

170 3.3. Photocatalytic decomposition of organic without sulphur in the chemical structure

171 The decomposition of Rhodamine 6G (C₂₈H₃₁ClN₂O₃, abbreviated as R6G), which is a
 172 dye without sulphur in its structure, was examined in the presence of Ca²⁺ (by adding CaCl₂ or
 173 Ca(COOCH₃)₂ into the solution). It was reported that nitrate ions can interact with R6G to
 174 show the decrease of the concentration [39], so that calcium nitrate was not used to examine
 175 the decomposition of R6G in the present study. The changes in the concentration by the UV
 176 irradiation are shown in Fig. 4. The decomposition of R6G was not accelerated by the presence

177 of Ca^{2+} , supporting the important role of the *in-situ* removal of the sulphur containing species
178 on the photodegradation of sulphur containing organics.



179

180 Fig. 4. Photocatalytic decomposition of R6G in the absence and the presence of Ca^{2+} by adding
181 CaCl_2 or $\text{Ca}(\text{COOCH}_3)_2$ in the solution.

182 3.4. Proposed mechanism for the accelerated photodegradation of sulphur containing organics

183 Precipitate was clearly observed as the sediment after the decomposition of MB in the
184 presence of Ca^{2+} (Fig. 5a), while the amount of the precipitate was too small to be collected for
185 its identification. The amount of CaSO_4 which may be formed considering the sulfate anions
186 resulting from MB oxidation, is estimated to 0.13 mg based on the stoichiometric calculation
187 assuming the complete decomposition of the MB in the starting solution. The presence of
188 sulfate ions formed in the solution after the decomposition of MB in the presence of Ca^{2+} and
189 Na^+ for 16 h (colorless solutions) was examined by ion chromatography, as shown in Fig. 5b.
190 The concentration of sulfate ions in the solution containing Ca^{2+} and Na^+ were 0.4 and to 6.4
191 mg.L^{-1} , respectively. Assuming the complete decomposition of MB, the estimated

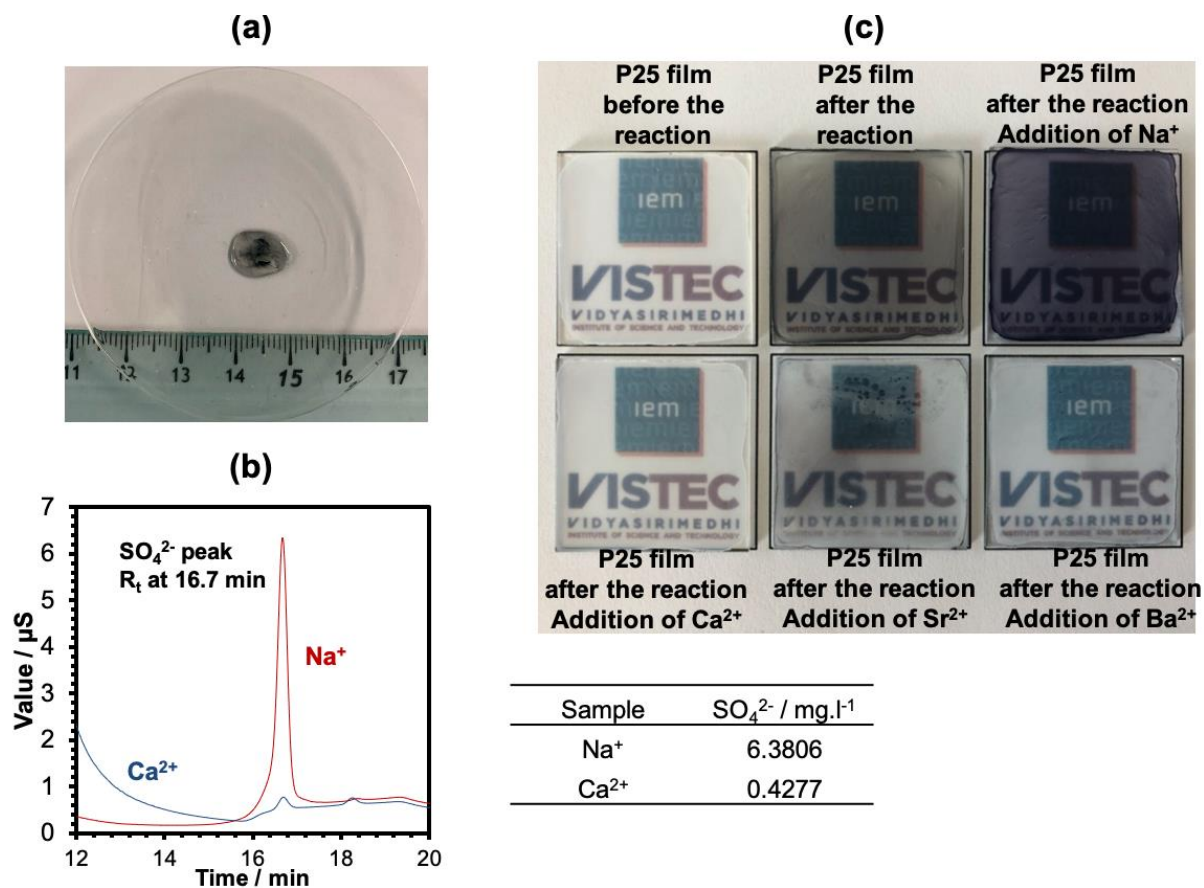
192 concentration of sulfate ions in the solution is 9 mg.L⁻¹. It was thought that the sulfate ions
193 were removed from the solution by the precipitation with Ca²⁺ as CaSO₄.

194 The concentration of sulfate ions required for the formation of alkaline earth sulfates is
195 calculated to be 4.6, 0.05, and 2.1×10⁻⁵ mg.L⁻¹ for CaSO₄, SrSO₄ and BaSO₄, respectively,
196 from solubility equilibrium's equation using the initial concentration of alkaline earth cations
197 (0.5 mol.L⁻¹) and the solubility product constant (K_{sp}) of 2.4×10⁻⁵, 2.51×10⁻⁶, and 1.07×10⁻¹⁰
198 for CaSO₄, SrSO₄ and BaSO₄ [40,41], respectively. Those values were lower than the expected
199 concentration of sulfate ions in the present experiment after the complete decomposition of MB
200 (ca. 9 mg.L⁻¹), meaning that the precipitation of CaSO₄, SrSO₄ and BaSO₄ was possible from
201 the concentration of the sulfate ions formed by the decomposition of MB.

202 The observed effect of the additives on the improved efficiency of the degradation of
203 sulphur containing organics (AY42 and MB) is proposed to be a “chemical equilibrium shift”,
204 where the product (sulfate) was removed during the reactions by the alkaline earth cations
205 (Ca²⁺, Ba²⁺, and Sr²⁺) as sulfate precipitation. The presence of the precipitates and the loss of
206 sulfate ions in the solution during the irradiation are the evidences of the removal of S oxide
207 species as metal (Ca²⁺, Ba²⁺, and Sr²⁺) sulfates.

208 In addition to the equilibrium shift concept, the deactivation of TiO₂ by the adsorption
209 of S oxide species was suppressed as another positive aspect of the present strategy. The film
210 was re-used to obtain the similar results for the MB decomposition in the absence and the
211 presence of Ca²⁺ (Fig. S2). The efficient MB decomposition was found in the second and third
212 runs in the presence of Ca²⁺, while the decomposition of MB was retarded when the P25 film
213 was re-used for the reaction in the absence of Ca²⁺. These were consistent with the relatively
214 white color of the P25 film after the reactions in the presence of Ca²⁺, Sr²⁺, and Ba²⁺, when
215 compared with the P25 film after the reactions without adding such ions as Ca²⁺, Ba²⁺, and
216 Sr²⁺, or in the presence of Na⁺ (Fig. 5c). Therefore, the simultaneous prevention of S oxide

217 species adsorption on the catalysts and the efficient removal of product (as sulfates) are
 218 clarified as two possible mechanisms on the acceleration of MB decomposition.



219
 220 Fig. 5. (a) Photograph of precipitated powder after the decomposition of MB in the presence
 221 of Ca^{2+} . (b) Characterization of sulfate ions remaining in the solution by Ion Chromatography.
 222 (c) Photographs of the P25 film before and after the reaction.

223 The effects of the added inorganic cations (such as K^{+} , Na^{+} , Ca^{2+} and Mg^{2+}) [42-49]
 224 and anions (such as Cl^{-} , SO_4^{2-} and NO_3^{-}) [50-57] on the decomposition of various organics have
 225 been reported in the literature, where the reactions were conducted in aqueous TiO_2
 226 suspensions. For the reactions in the presence of Ca^{2+} , no significant acceleration was found on
 227 the decomposition of phenol [42,43], crystal violet [44], and glyphosate [45], while negative
 228 effects were observed for the decomposition of rhodamine B [46], nicosulfuron [47], and
 229 formic acid [48]. The adsorption of the added inorganic cation (Ca^{2+}) and anions (SO_4^{2-}) onto

230 the photocatalyst (TiO₂) was claimed as a reason of the inhibition of the decomposition of
231 nicosulfuron by blocking the accessible surface of TiO₂. The sedimentation of P25 was
232 observed in the aqueous suspension by the addition of Ca²⁺ salts (Fig. S1). The sedimentation
233 of P25 in the aqueous suspension is thought to affect the decomposition rate of MB by losing
234 the active surface for the reaction by the aggregation of P25 and also by increasing the diffusion
235 path from the solution to the active surface in the core of the formed aggregates as well as the
236 loss of incident light propagation. Thus, the decomposition efficiency in the aqueous
237 suspension of TiO₂ is difficult to be directly compared with the result achieved in the present
238 study by using P25 film as the photocatalysts. The application of P25 film in this work is a key
239 from the viewpoint of the product characterization.

240 **4. Conclusions**

241 The decomposition of the sulphur containing organics (MB and AY42) was
242 successfully accelerated for the first time by adding inorganic cations (alkaline earth cations)
243 to capture the S oxide species (as sulfates) formed during the decomposition. Since the
244 commonly used suspension of photocatalysts cause the aggregation during the reaction, the
245 film of P25 supported on borosilicate glass was used as the photocatalyst, which was a key of
246 the present success. The acceleration was explained by the two mechanisms, equilibrium shift
247 and the suppressed poisoning (deactivation) of the catalyst's surface with sulfate. The present
248 concept (*in-situ* removal of a product) can be applied various photocatalytic reactions to be
249 accelerated.

250 **CRedit authorship contribution statement**

251 **Siwada Deepracha:** Methodology, Formal analysis, Investigation, Writing – Original
252 Draft, Writing – Review & Editing. **André Ayrál:** Validation, Formal analysis, Resources,

253 Writing – Review & Editing. **Makoto Ogawa:** Conceptualization, Validation, Writing –
254 Review & Editing, Supervision.

255 **Declaration of Competing Interest**

256 The authors declare that they have no known competing financial interests or personal
257 relationships that could have appeared to influence the work reported in this paper.

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264 on SEM observation.

265 **Appendix A. Supplementary data**

266 Photocatalytic decomposition of MB by the P25 dispersed in the aqueous MB solution
267 with and without addition of $\text{Ca}(\text{NO}_3)_2$, photograph of the P25 dispersed in water with and
268 without addition of $\text{Ca}(\text{NO}_3)_2$, and reuse of the photocatalyst film for the photocatalytic
269 decomposition of MB

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