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# Effects of water environmental factors on the photocatalytic degradation of sulfamethoxazole by AgI/UiO-66 composite under visible light irradiation

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#### ABSTRACT

It is necessary to find visible light responsive photocatalysts for rapid and simple degradation of organic pollutants in water environment. In this work, a visible light responsive composite photocatalyst Agl/ UiO-66 was prepared by an in situ growth method. Sulfamethoxazole (SMZ) antibiotic was selected as the target contaminant to probe the photocatalytic performance of the as-prepared AgI/UiO-66 composite under visible light irradiation. The results showed that the photocatalytic performance of the Agl/ UiO-66 composite enhanced significantly compared to pure AgI. The effects of typical environment factors (i.e. pH, inorganic salt ions and common anions) on the degradation of SMZ were evaluated extensively. Results showed that the investigated pH (5.2, 7.0, 9.5) had no apparent effect on the photocatalytic degradation of SMZ except pH 2.5, at which the degradation rate of SMZ decreased significantly. In addition, inorganic salt ions and  $Cl^-$ ,  $HCO_3^-$  and  $SO_4^{2-}$  anions in water exhibited no apparent effect on the degradation of SMZ. The effect of water matrix on the degradation of SMZ was also investigated. In the river water, the removal efficiency of SMZ was reduced compared with the cleaner water matrix. The capture experiments of radicals confirmed that superoxide radicals ( $\cdot O_2^-$ ) and hydroxyl radicals (•OH) were the main active species for the photocatalytic degradation of SMZ in the present work. Finally, the tentative degradation pathways of SMZ were proposed based on the intermediates analysis.

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#### 1. Introduction

The pollution problem of antibiotics in environment has aroused widespread concern in society. Sulfonamide is one type of the most widely used antibiotics in human and veterinary drugs. Each year a large number of sulfonamides enter the environment [1-3]. Sulfonamides are known as trace contaminants in water environment that are difficult to be degraded, thus cause drug resistance for human and environmental organisms. As one of the most widely detected sulfonamides in water, sulfamethoxazole (SMZ) has been investigated in many studies as a sulfonamide antibiotic model for its universality, persistence and toxicity [4,5]. Therefore, it is extremely imperative for human to effectively eliminate SMZ

antibiotics.

At present, common methods of removing antibiotics in water include biological treatment [6,7], active carbon adsorption [8], photocatalysis [9,10] and ozone oxidation method [11]. In these water treatment technologies, photocatalytic technology attracts more and more attention. Photocatalysis can quickly and effectively degrade organic pollutants in mild environment without secondary pollution [12,13]. In particular, photocatalytic applications in visible light will be the most attractive, because it can use readily available sunlight [14]. Therefore, it is necessary to develop a semiconductor material with high visible light utilization efficiency.

AgI is a visible light driven photocatalyst and its excellent photocatalytic performance has attracted considerable attention [15–17]. AgI can absorb photons to produce electron-hole pairs under visible light irradiation. But AgI is unstable and is easily reduced to Ag under visible light irradiation [18]. If AgI is dispersed on some carriers, it can maintain stability while preventing the occurrence of photocorrosion because of the fast transferring of







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charges [19]. On the other hand, the metal organic frameworks (MOFs) material has been widely used in the photocatalytic process because of its high specific surface area, adjustable aperture and good stability [20–22]. In particular, UiO-66, a Zr-based MOF has been extensively used for photocatalysis. UiO-66 not only exhibits high structural stability [23], but maintains such stability after the modification of active functional groups or the introduction of missing joint defects [24]. These properties make UiO-66 a particularly prospective candidate for photocatalytic applications in water treatment. This creates a motivation to exploit UiO-66 based photocatalysts for water treatment. Hence, the UiO-66 with high specific surface area was selected as the support to control the growth of AgI.

In this article, AgI nanoparticles were grown in situ on the UiO-66 framework. The phase structures, morphologies and optical properties of the prepared catalysts were detected. Moreover, the effects of water environmental factors (pH value, inorganic salt ions, common anions and water matrix) on the degradation of SMZ were discussed. In addition, the photocatalytic mechanism of SMZ was also investigated, including active substances, oxidation products and degradation pathways.

#### 2. Materials and methods

#### 2.1. Reagent

Zirconium tetrachloride, terephthalic acid, N, *N*-dimethyl formamide, methanol, potassium iodide, argentum nitricum, hydrochloric acid (HCl), sodium hydroxide (NaOH), sodium chloride, sodium sulfate, sodium bicarbonate, ferric chloride, calcium chloride, magnesium chloride and potassium chloride were purchased from Sinopharm (China). SMZ was purchased from Aladdin (America). Pure water was acquired from a purification system (Millipore Milli-Q, USA). Acetonitrile and formic acid were supplied by Tedia (America), and they were chromatographic pure reagents. Other reagents were all analytical reagents.

#### 2.2. Preparation of material

#### 2.2.1. Preparation of UiO-66

UiO-66 was synthesized by modified solvothermal method [25]. Zirconium tetrachloride (2.0 mmol) and terephthalic acid (2.0 mmol) were successively dissolved in N, *N*-dimethyl formamide (100 mL) and the solution was transferred into a 200 mL of stainless steel autoclave. The autoclave was sealed and heated in a 120 °C oven for 24 h. After natural cooling, the precipitate was centrifuged and immersed in methanol for three days. Methanol was changed every 24 h. Finally, the white products were dried under vacuum at 60 °C.

#### 2.2.2. Preparation of AgI/UiO-66

Potassium iodide (153 mg) was dissolved in 45.5 mL of pure water. Then, UiO-66 (250 mg, structural formula noted as  $Zr_{24}O_{120}C_{192}H_{96}$  [26]) was added into the above solution under vigorous stirring. After stirring for 1 h, 4.61 mL of 0.2 M AgNO<sub>3</sub> aqueous solution was added into the above mixture solution and kept stirring at room temperature for 12 h. Next, the products were collected by centrifugation and washed thoroughly with pure water for several times. Ultimately, the obtained samples were dried under vacuum at 60 °C.

#### 2.3. Characterization

The X-ray diffraction patterns of the samples were analyzed by Rigaku's SmartLab diffractometer in the range of  $2\theta$  between 5° and

50°. The morphology features of as-prepared samples were observed by transmission electron microscopy (TEM, FEI, TECNAI G20). The optical properties of the samples were researched using UV–Vis diffuse reflectance spectroscopy (Shimadzu, UV3600).

#### 2.4. Photocatalytic experiments

#### 2.4.1. Photocatalytic degradation of SMZ

In this experiment, 25 mg of the as-prepared sample was added to 50 mL of 5 mg/L SMZ aqueous solution and kept in dark conditions for 1 h to achieve adsorption equilibrium. Then the mixture solution was irradiated by a 300 W Xe lamp (Beijing Zhongjiaojinyuan, CEL-HXF300) with a 400 nm cut-off glass filter. After the start of the illumination, 1.5 mL of the solution was taken at regular intervals and filtered with a 0.22  $\mu$ m syringe filter to remove the suspended solid particle before the detection of the concentration of SMZ. The blank experiment of SMZ photolysis was the same as above procedure except that no catalyst was added. The environmental factor experiment was carried out by the similar procedure.

#### 2.4.2. Trapping experiments of active species

The trapping experiments were carried out under the same reaction conditions except that the capture agent was added into the photocatalytic reaction solution. The active species were •OH,  $\cdot O_2^-$  and  $h^+$  which were captured by tert-butanol (5 mmol/L), *p*-benzoquinone (1 mmol/L) and EDTA-2Na (5 mmol/L) respectively.

#### 2.5. Analysis methods

The concentration of SMZ was detected by high performance liquid chromatography (HPLC, Waters e2695) with a UV detector at 270 nm. The chromatographic column was reversed phase C18 column (4.6 mm  $\times$  150 mm, 5  $\mu$ m). The mobile phase was 30% acetonitrile and 70% water (pH = 3) adjusted with phosphoric acid at a flow rate of 1 mL/min. The injection volume was 10  $\mu$ L and the column temperature was maintained at room temperature during injection analysis.

The intermediates produced during the degradation of SMZ were identified via liquid chromatography-triple quadrupole mass spectrometry (LC-MS, Agilent, 6460 Triple Quad LC/MS series) with a C18 column (2.1 mm  $\times$  50 mm, 1.8  $\mu$ m). The chromatographic conditions of the HPLC were shown as follows: the flow rate was 0.2 mL/min and the column temperature was 25  $^{\circ}$ C with 5  $\mu$ L of the injection volume. The mobile phase was aqueous solution A containing 0.1% formic acid and acetonitrile B containing 0.1% formic acid. The gradient elution program was presented as follows: 0-3 min, 10%-20% B, 3-8 min, 20%-35% B, 8-15 min, 35%-60% B, then equilibrated for 6 min. An electrospray ionization source API-ES was used for MS/MS measurements in the positive ion mode and full spectrum scanning. The other parameters were set as follows: the capillary voltage was 3000 V. The atomization pressure and the drying gas temperature were 30 psi and 300 °C, respectively, and the flow rate of dry gas was 10 L/min.

#### 3. Results and discussion

#### 3.1. Characterization

In order to more clearly observe the appearance of the sample, we conducted TEM and HRTEM characterization. It can be seen from Fig. 1(a) that UiO-66 is a regular cube structure. In Fig. 1(b) and (c), several nanometers to dozens of nanometers of small particles adhere to the surface of UiO-66 and grow around UiO-66. In addition, Fig. 1(d) showed that 0.210 nm and 0.225 nm lattice edge spacing correspond to 103 and 110 lattice planes of Agl nanocrystals.



Fig. 1. TEM images of pure UiO-66 (a) and AgI/UiO-66 composites (b, c), HR-TEM image of AgI/UiO-66 (d).

It can be judged that these small particles are AgI nanoparticles. The results indicate the formation of AgI/UiO-66 composite.

Fig. 2 shows the XRD patterns of pristine UiO-66, AgI and AgI/UiO-66 composite. The main diffraction peaks of pure AgI at the  $2\theta$  of  $22.3^{\circ}$ ,  $23.7^{\circ}$ ,  $25.4^{\circ}$ ,  $32.7^{\circ}$ ,  $39.2^{\circ}$ ,  $42.6^{\circ}$ ,  $45.6^{\circ}$ ,  $46.3^{\circ}$  and  $47.2^{\circ}$  correspond to (100), (002), (101), (102), (110), (103), (200), (112) and (201) planes, respectively. These peaks are well matched with AgI crystals (JCPDS card 09–0374) [19], indicating that they are well crystallized. The XRD pattern of the pure UiO-66 is corresponding to the results reported in the previous literature [26]. In addition, the composite AgI/UiO-66 exhibits a new diffraction peak compared to the pure UiO-66, which is consistent with the diffraction peaks of pure AgI. The major diffraction peaks of UiO-66 are clearly visible in the XRD pattern of AgI/UiO-66 composite, thus demonstrating the successful synthesis of AgI/UiO-66 samples.

The UV-vis diffuse reflection was tested to probe the optical properties of the sample and the obtained results are shown in Fig. 3(a). Obviously, it is observable that the absorption edge of pure UiO-66 is at 340 nm thus it can only absorb ultraviolet light. The



Fig. 2. XRD patterns of as-prepared samples.



Fig. 3. UV-Vis diffuse reflectance spectroscopy (a) and energy band (b) for different samples.

pure AgI has a 470 nm absorption edge that responds to visible light. Moreover, compared with the absorption spectrum of pure UiO-66, AgI/UiO-66 composite exhibits a red shift and has absorption edges at about 460 nm. It turns out that the synthesized composites have good visible light absorption. The bandgap energy of the as-prepared samples can be calculated through the following formula:  $ahv = A(hv-Eg)^{n/2}$ , where a, h, v, Eg and A are the absorbance. Planck constant, optical frequency, bandgap energy and constant, respectively [27]. The n value is chosen by the type of optical conversion of the semiconductor, where the n value of the semiconductors directly allowed to be converted is 1, and the value of n for indirect forbidden conversion of semiconductors is 4. Both UiO-66 and AgI have direct strip transition characteristics, so the n value of them is 1. As a result, the bandgap of UiO-66, AgI and AgI/ UiO-66 samples are represented by (ahv)<sup>2</sup> relative (hv) graphs, as shown in Fig. 3(b). The Eg of UiO-66 and AgI are estimated to be 3.90 eV and 2.80 eV which are approximate to the values reported in the previous literature [28,29]. The Eg of AgI/UiO-66 sample is 2.82 eV which indicates its visible light absorption properties.

#### 3.2. Photocatalytic degradation of SMZ

The photocatalytic experiments were carried out in the pure aqueous solution of SMZ with natural pH of 5.2. Fig. 4(a) shows the



**Fig. 4.** The photocatalytic degradation of SMZ by different samples, inset: adsorption curve of SMZ by different photocatalysts (a), reaction rate constant k of as-prepared samples (b) (initial concentration = 5 mg/L, photocatalysts = 0.5 g/L, natural pH).

photocatalytic degradation plot of SMZ in the presence of different samples. It can be seen that there is no degradation of SMZ under visible light without any photocatalyst in 20 min. Furthermore, the adsorption curves of SMZ by different photocatalysts are presented in the inset of Fig. 4(a). It is available that the adsorption percent were 11.7%, 1.35%, 6.69%, 15.3% for UiO-66, AgI, physical mixture and AgI/UiO-66, respectively. Then the order of degradation percent of SMZ by different samples can be clearly seen as follows: AgI/UiO-66 > AgI > physical mixture > UiO-66. The pure UiO-66 did not substantially degrade SMZ under visible light because UiO-66 only had a UV response. In addition, due to the presence of AgI, the degradation percent of physical mixture is slightly higher than the pure UiO-66.83.8% of SMZ was degraded by AgI in 20 min. However, over 99.6% of SMZ was degraded by AgI/UiO-66 composites in 20 min. The kinetic curve of these samples can be used to represent the photocatalytic degradation performance for different samples. The first-order kinetic model is used to fit the data shown in Fig. 4(a):  $\ln (C_0/C) = kt$ . And the corresponding rate constants k is shown in Fig. 4(b). The apparent rate constant k values of pure UiO-66, AgI, AgI/UiO-66 composite and physical mixture sample are 0.00095, 0.066, 0.32 and 0.0099 respectively. The rate constant k of AgI/UiO-66 composite is 4.8 times higher than that of pristine AgI, which signifies that the photocatalytic performance of AgI/UiO-66 composites was significantly higher than that of pure AgI. The results indicated that the deposition of AgI onto UiO-66 enhanced the photocatalytic activity significantly. It can be described to the following reasons: (1) In the AgI/UiO-66 composite, UiO-66 is used as a carrier to cause the high dispersion of AgI and increase the amount of AgI active sites, thus enhancing the photocatalytic activity of AgI [30]; (2) the good interaction between AgI and UiO-66 may contribute to the transfer of electrons from AgI to UiO-66 in a way. This interaction can prevent corrosion of AgI by photogenerated electrons and further improve the photocatalytic activity of AgI/UiO-66.

The stability and reusability of the photocatalyst is a crucial factor for practical applications. In order to assess the stability and reusability of the Agl/UiO-66 composite, the cycling experiment was performed in same photocatalytic reaction conditions, and the results are presented in Fig. 5. After four cycles, the degradation rate of SMZ can also reach more than 99%. It demonstrates that the Agl/UiO-66 composite has good stability and reusability through multiple degradation.



**Fig. 5.** Cycling experiments of Agl/UiO-66 composites for the photocatalytic degradation of SMZ (initial concentration = 5 mg/L, Agl/UiO-66 = 0.5 g/L, natural pH).



**Fig. 6.** Effects of pH on SMZ degradation by Agl/UiO-66 composite under visible light irradiation (initial concentration = 5 mg/L, Agl/UiO-66 = 0.5 g/L, pH = 2.5, 5.2, 7.0 and 9.5).

# 3.3. Effects of water environmental factors on the photocatalytic degradation of SMZ

#### 3.3.1. pH

The concentration of H<sup>+</sup> in water (i.e pH) can affect the production and distribution of oxidized substances during the photocatalytic degradation process. The photocatalysis experiments were carried out in SMZ aqueous solutions at pH 2.5, 5.2, 7.0 and 9.5, respectively. The pH was adjusted with dilute hydrochloric acid and sodium hydroxide. It can be seen from Fig. 6 that the SMZ has a high degradation efficiency in pure aqueous solution with a natural pH of 5.2. Because at this pH value, SMZ exists mainly in the form of neutral molecules which have strong light absorption and high photochemical reactions [31]. In a solution with a pH of 7, SMZ is presented as an anionic form and the photocatalytic degradation of the drug is inhibited at the initial stage. However, as the illumination time was prolonged, the inhibition effect is gradually weakened and the photocatalytic activity is gradually improved. The results are in good agreement with previous papers [32,33]. Compared with the initial solution (pH = 5.2), the degradation rate



**Fig. 7.** The impact of Cl<sup>-</sup>,  $HCO_3^-$  and  $SO_4^{2-}$  anions on SMZ degradation (initial concentration = 5 mg/L, Agl/UiO-66 = 0.5 g/L, natural pH).



**Fig. 8.** Effects of inorganic salt ions on SMZ degradation by Agl/UiO-66 composite under visible light irradiation (initial concentration = 5 mg/L, Agl/UiO-66 = 0.5 g/L, natural pH).

of SMZ was not significantly changed in the alkaline solution. In acidic solution, the degradation percent of SMZ was distinctly decreased. As we know, in the photocatalytic reaction, dissolution oxygen combined with photo-generated electrons will produce  $\cdot O_2^-$  (eq. (1)). The acidic solution contains a large amount of H<sup>+</sup> which will consume the solution of  $\cdot O_2^-$ . And from the trapping experiments can be seen that  $\cdot O_2^-$  was the most important active species in the photocatalytic degradation process. In the acidic aqueous solution,  $\cdot O_2^-$  combined with a large number of H<sup>+</sup> (eq. (2)) in the presence of photo-generated electrons to produce H<sub>2</sub>O<sub>2</sub>. Finally, H<sub>2</sub>O<sub>2</sub> is converted into  $\cdot OH$  (eq. (3) and eq. (4)) to continue the photocatalytic reaction [34].

$$\mathbf{0}_2 + \mathbf{e}^- \to \mathbf{0}_2^- \tag{1}$$

$$\bullet O_2^- + 2H^+ + e^- \to H_2O_2$$
 (2)

$$H_2O_2 + e^- \rightarrow \bullet OH + OH^- \tag{3}$$

$$h^{+} + OH^{-} \rightarrow \bullet OH \tag{4}$$



Fig. 9. Degradation profiles of SMZ in different water matrix (initial concentration = 5 mg/L, Agl/UiO-66 = 0.5 g/L).



**Fig. 10.** The capture experiments of SMZ under visible light irradiation (initial concentration = 5 mg/L, Agl/UiO-66 = 0.5 g/L, natural pH).

#### 3.3.2. Inorganic anions

The general inorganic anions  $Cl^-$ ,  $HCO_3^-$  and  $SO_4^{2-}$  in the surface water would have an effect on the removal efficiency of target pollutants. Thus, their effects on the photocatalytic degradation of SMZ were studied by adding the same amount of 5 mM NaCl, NaHCO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub> to the photocatalytic reaction solution. Fig. 7 shows that the addition of  $Cl^-$  and  $SO_4^{2-}$  has practically little influence on the degradation of SMZ compared to the reaction process in pure water. The presence of Cl<sup>-</sup> can form inorganic free radicals  $Cl_{\cdot}$  and  $Cl_{2}$ , which can also induce the decomposition of SMZ. Previous studies have shown that  $Cl_{2}$  and  $Cl_{2}$  can react with contaminants in water, and the reaction rate constant is at the same level as •OH [35]. When the sulfate was added, the degradation rate was slightly increased. The possible reason is that the sulfate anion free radical can oxidize organic molecules. On the other hand, the addition of  $SO_4^{2-}$  may promote the formation of •OH [1]. However, the degradation rate was significantly reduced after the addition of  $HCO_{\overline{3}}$  into the reaction solution.  $HCO_{\overline{3}}$  is a robust hydroxyl radical scavenger with the reaction that occurs as follows:  $HCO_3^- + \bullet OH \rightarrow CO_3^- + H_2O$  [36].  $\bullet OH$  is important active species of

photocatalytic reactions, which are known from the capture experiments. And  $\cdot CO_3^-$  is a weaker oxidizing agent than •OH. As the reaction progresses, •OH is captured thus affecting the photocatalytic degradation of SMZ.

#### 3.3.3. Inorganic cation

The effect of different metal cations on the degradation of SMZ was investigated under the presence of Cl<sup>-</sup>. 5 mM equivalent FeCl<sub>3</sub>, MgCl<sub>2</sub>, CaCl<sub>2</sub>, NaCl and KCl inorganic salts were added into the photocatalytic reaction solution and the photocatalytic degradation plots of SMZ are displayed in Fig. 8. It can be concluded that these ion salts have no inhibitory effect on the degradation of SMZ by Ag1/UiO-66. In the presence of these cations, SMZ was completely degraded in 15 min. Since the presence of chloride ions forms Cl- and Cl<sub>2</sub>·<sup>-</sup>, the progress of the reaction is facilitated. In general, these cations have little influences on the photocatalytic process.

#### 3.3.4. Waters matrix

Four different types of water matrix (pure water, mineral water, tap water, river water) were selected as the target solution for photocatalytic reaction. As observed from Fig. 9, in the three water environments of pure water, mineral water and tap water, the SMZ was almost completely degraded by AgI/UiO-66 in 15 min. The degradation efficiencies of SMZ in mineral water and tap water are similar to that of pure water. As discussed in section 3.3.2, the existing Cl<sup>-</sup> in tap water can form inorganic free radicals Cl· and  $Cl_2$ , which can also induce the decomposition of SMZ. Mineral water contains calcium, potassium and other minerals, whereas pure water is basically no impurities. From the analysis in section 3.3.3, it can be seen that calcium and potassium cations do not restrain the degradation of SMZ in the photocatalytic reaction. However, the degradation rate of SMZ is decreased significantly in the river water compared to that in pure water. It can be ascribed to the fact that the groups of the natural organic matter in the river water may react with •OH to inhibit the degradation of SMZ [37].

#### 3.4. Photocatalytic mechanism

3.4.1. Trapping experiments of active species

As shown in Fig. 10, the addition of EDTA-2Na did not



Fig. 11. The schematic diagram of SMZ photocatalytic degradation mechanism by Agl/UiO-66 composite under visible light irradiation.



Fig. 12. Proposed degradation pathways of SMZ by AgI/UiO-66 composites under visible light irradiation.

significantly affect the degradation of SMZ, which indicated that the hole had little effect in the photocatalytic degradation reaction. Furthermore, the degradation of SMZ was obviously inhibited when *p*-benzoquinone was added as a trapping agent of  $\cdot O_2^-$ . At the same time, it also demonstrated that  $\cdot O_{\overline{2}}$  is the predominant active species in the degradation process of SMZ. When tert-butanol was added, the degradation efficiency of SMZ was also decreased. This reveals that SMZ can be oxidized by •OH in the AgI/UiO-66 photocatalyst system. Consequently,  $\cdot O_2^-$  and  $\cdot OH$  are the major active species in the photocatalytic degradation of SMZ by the AgI/UiO-66 composites. Based on the above results, the possible mechanism for the degradation of SMZ by AgI/UiO-66 composite is shown in Fig. 11. The AgI nanoparticles grow on the surface of UiO-66 frameworks, which prevent the agglomeration of AgI particles. Under the visible light irradiation, the electrons on the surface of AgI can migrate from the valence band to the conduction band. Then the electrons are captured by dissolved oxygen in water to produce  $\cdot O_2^-$ . On the other hand, the holes promote the generation of •OH. Both  $\cdot O_2^-$  and •OH can oxidize SMZ [38].

#### 3.4.2. Identification of intermediates

In order to understand the degradation process of SMZ more explicitly, the LC/MS/MS analysis was conducted to identify the intermediates of SMZ. The degradation pathway of SMZ and the molecular structure of intermediates are presented in Fig. 12 and Table 1, respectively.

Generally m/z 254 protonated molecular ion  $[M+H]^+$  is chosen as SMZ precursor ion (noted as m/z = 254 $[M+H]^+$ ) [39,40]. The first pathway of the SMZ decomposition process is that the amino group on the benzene ring is oxidized to form nitro groups, and the resulting product is labeled as P1 (m/z = 284 $[M+H]^+$ ). The second pathway is the hydroxylation of the isoxazole ring. The breakage of *N*-O bond on the isoxazole ring leads to the formation of products P2 (m/z = 272  $[M+H]^+$ ) and P3 (m/z = 288  $[M+H]^+$ ). The P1, P2 and P3 products will continue to be attacked by •OH and induce S–N bond breakage to further form sulfanilic acid, and the product is

Table 1

The possible intermediates during the photocatalytic degradation process by Agl/UiO-66 composites under visible light irradiation.

Product	RT/min	m/z([M+H] <sup>+</sup> )	Formula	Proposed structure
SMZ	9.08	254	C <sub>10</sub> H <sub>11</sub> N <sub>3</sub> O <sub>3</sub> S	
P1	4.80	284	$C_{10}H_9N_3O_5S$	
Р2	8.87	272	C <sub>10</sub> H <sub>13</sub> N <sub>3</sub> O <sub>4</sub> S	
Р3	10.6	288	$C_{10}H_{13}N_3O_5S$	
Р4	1.08	99	$C_4H_6N_2O$	H <sub>2</sub> N-O
Ρ5	1.2	174	C <sub>6</sub> H <sub>7</sub> NO <sub>3</sub> S	

signed as P5 (m/z = 174[M+H]<sup>+</sup> [33]). In addition, SMZ molecules can directly hydrolysis under the visible light irradiation. The unstable S–N bond on SMZ is broken and then P4 (m/z = 99 [M+H]<sup>+</sup>) and P5 products are generated. The resulting products P4 and P5 have relatively small molecular mass, simple structure, which will be further decomposed to CO<sub>2</sub> and H<sub>2</sub>O by •OH and •O<sub>2</sub><sup>-</sup> radicals.

#### 4. Conclusions

In this study, AgI/UiO-66 was prepared by an in situ growth method. The as-prepared AgI/UiO-66 composite presents a high photocatalytic performance for the degradation of SMZ under visible light irradiation. The SMZ in the weak acid, weak alkali and neutral environment can be degraded completely in 20 min by the AgI/UiO-66 composites under the visible light irradiation. However, photocatalytic performance was obviously reduced under acidic conditions. And the degradation of SMZ was slightly impacted by the environment of inorganic salts and  $Cl^-$ ,  $HCO_3^-$  and  $SO_4^{2-}$  anions. In addition, SMZ was decomposed with similar rate in pure water, tap water and mineral water. However, the degradation efficiency decreased in river water apparently. The main active species that responsible for the degradation of SMZ were recognized as  $\cdot O_2^-$  and •OH through trapping experiments. The degradation pathway of SMZ is separated into three parts, namely, phenyl nitrification, isoxazole ring hydroxylation and S-N bond cleavage. Finally, SMZ antibiotic was converted into two small molecules of oxidation products which could be further decomposed to CO<sub>2</sub> and H<sub>2</sub>O.

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