Photocatalytic degradation kinetics and mechanism of environmental pharmaceuticals in aqueous suspension of TiO$_2$: A case of sulfa drugs

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**Article info**

The photocatalytic degradation kinetics of three sulfa pharmaceuticals has been investigated in TiO$_2$ aqueous suspension. The disappearance of these three compounds follows a pseudo-first-order kinetics according to the Langmuir–Hinshelwood (L–H) model. The effects of catalyst amount, initial pH value, and initial concentration of each substrate on the photocatalytic degradation rates were measured in detail. It was observed that the surface reaction on TiO$_2$ played an important role in the degradation of sulfa pharmaceuticals, and the further study of reactive oxygen species (ROSs) indicated that both photohole (h$^+$) and especial hydroxyl radical (•OH), were responsible for the major degradation of sulfa pharmaceuticals. The fates of the sulfur and nitrogen elements in various sulfa pharmaceuticals as well as total organic carbon (TOC) were examined following their photocatalytic transformation. The data showed that all three pharmaceuticals could be completely mineralized into CO$_2$, H$_2$O and inorganic ions within 240 min. These results indicated that many intermediates were produced during the photocatalytic transformation of sulfa pharmaceuticals process. Based on the identified intermediates, two tentative degradation pathways for the photocatalytic degradation of sulfa pharmaceuticals were proposed, for example hydroxylation addition to parent pharmaceuticals and the cleavage of S–N bond from the sulfanilic acid attacked by photohole.

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1. Introduction

The presence of pharmaceuticals and personal care products (PPCPs) in surface water is an emerging environmental issue and provides a new challenge to drinking water, wastewater, and water reuse treatment system [1–4]. One class of antibiotics pharmaceuticals, sulfa drugs, is frequently found in the environmental waters, such as sewage treatment plants water [5–7] and river [8]. Several recent researches also demonstrated the potential omnipresence of sulfa pharmaceuticals in the soil environment [9] and manure [10–13]. It is because sulfa pharmaceuticals are often used in aquaculture [14], agriculture as herbicides and veterinary pharmaceuticals [15,16], and human beings for the treatment of respiratory and urinary tract infections [17]. However, due to their high resistance to the photodegradation [17–20] and biodegradation [21,22], these kinds of pharmaceuticals were often excreted into sewage with metabolites as well as the unchanged parent compounds after usage [23]. These discharged sulfa pharmaceuticals could persist in environmental waters for a long time and accumulate in various organisms of the food chain [24,25], which may adversely affect the environmental ecosystems [26] and human health [27]. Although these kinds of sulfa pharmaceuticals have been used for several decades, it is surprising that there are only few studies to investigate their environmental and health effect. Thus, it is very essential to study the transformation kinetics and mechanism involved in various environmental conditions. By doing this, their environmental fate, transfer, effect and potential risk of these kinds of sulfa pharmaceuticals can be properly elucidated in environmental waters as well as during water treatment processes.

Advanced oxidation processes (AOPs) are accepted as a valid alternative to transform and decontaminate these soluble biorefractory human antibiotics. These processes named AOPs all rely on the generation of highly reactive •OH radical as the main oxidative species for the potential destruction and conversion of organic pollutants into harmless substances [28–31]. Heterogeneous photocatalysis is one typical example of AOPs for the degradation of pharmaceuticals and other organic pollutants in water [32–35]. In recent years, although there are already a few researches to report the photocatalytic degradation possibility of sulfa pharmaceuticals, these works are still not so sufficient to fully understand the transformation kinetics and mechanism of these kinds of pharmaceuticals in water [36,37]. Thus the relationship between the

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2. Materials and methods

2.1. Chemicals and reagents

Sulfachlorpyridazine, sulfapyridine and sulfisoxazole (Sigma–Aldrich) were used as received (>99% purity, the structures are shown in Fig. 1). HPLC grade water was obtained from Millipore Milli-Q System (Water, Millipore), which was treated by constant illumination with a Xe arc lamp at 172 nm to keep total organic carbon concentration below 13 μg/L. Acetonitrile and methanol (HPLC grade) were purchased from Sigma.

2.2. Irradiation procedures

The adsorption and photocatalytic degradation of sulfa pharmaceuticals were carried out in a Pyrex reactor (150 mL) with a double-walled cooling–water jacket to keep the constant temperature of solutions throughout the experiments. The light source was a high-pressure mercury lamp (GGZ-125, Shanghai Yaming Light, 365 nm) with a power consumption of 125 W, housed in one side of the photocatalytic reactor to provide the irradiation. Prior to illumination, a suspension of 150 mL sulfa pharmaceuticals (100 μM) adding different concentrations of the photocatalyst (Degussa P25) was stirred in the dark for 30 min to achieve the adsorption–desorption equilibrium. Then, the UV light was turned on for the photocatalytic degradation experiments. Samples of the reaction solution (3 mL) were obtained at fixed time intervals, filtered through 0.2 μm Millipore filters and analyzed by HPLC and HPLC/MS/MS. All experiments were carried out at room temperature. The kinetic data are presented as means from triplicate experiments, and the errors are below 5%.

2.3. Analytical procedures

Photocatalytic degradation kinetics of sulfa pharmaceuticals was carried out by using an Agilent 1200 series HPLC under the following conditions: Kromasil C18 column, 250 mm × 4.6 mm i.d., performed at 30 °C. The mobile phase was 30% CH3CN and 70% formic acid solution (0.3%, v/v) which was filtered with a Water Associates (Milford, MA, USA) 0.45 μm filter. The flow rate of the mobile phase was set as 1 mL/min.

A Dionex instrument equipped with a conductimeter detector has been employed to analyze the concentration of produced anions and cations. The determination of ammonium ions has been performed by adopting a column CS12A and 25 mM H2SO4 as eluent, with a flow rate of 1 mL/min. The retention time is 5.2 min for ammonium ions. The anions have been analyzed by using AS9HC anionic column. The mixture of NaHCO3 (4.5 mM) and K2CO3 (0.8 mM) was used as eluent with a flow rate of 1 mL/min. The retention times are obtained as 11.7 min and 12.8 min for nitrate and sulphate, respectively. Total organic carbon (TOC) was measured after filtered suspensions using a Shimadzu TOC-5000 analyzer (catalytic oxidation on Pt at 680 °C).

Degradation intermediates were analyzed using an HPLC/MS/MS, a Shimadzu high performance liquid chromatography (HPLC) system with a Kromasil C18 column (250 mm × 4.6 mm i.d.), SIL-HT autosampler, LC-10 AT vacuum pump and API 3000 mass analyzer. HPLC separations were performed at 0.5 mL/min with linear gradient elution as follows: from 90% A (5 mM formic acid solution) and 10% B (CH3OH) to 40% A and 60% B within 40 min. An electrospray interface (ESI) was used for the MS and MS–MS measurements in positive ionization mode and full scan acquisition between m/z 100 and 350. The collision energy varied according to the requirement of the different measurements, and the other parameters were set as follows: the ESI was 5.5 keV, the source block and desolvation temperature were 130 °C and 400 °C, respectively, the desolvation and nebulizer gas (N2) flow rate were set as 6 L/min and argon was used as a collision gas at 2500 mbar.

3. Results and discussion

3.1. The photocatalytic degradation kinetics of sulfa pharmaceuticals

The photocatalytic degradation kinetics of three sulfa pharmaceuticals was investigated, and the results are shown in Fig. 2. After 60 min of illumination, the removal efficiencies were achieved as 85.2%, 92.5% and 85.0% for sulfachlorpyridazine, sulfapyridine and sulfisoxazole, respectively, with an initial concentration of 100 μM, a TiO2 concentration of 2.0 g/L and an initial pH value 7.0. The photocatalytic degradation of three sulfa pharmaceuticals can be well described by Langmuir–Hinshelwood (L–H) model [38]:

$$ \frac{dc}{dt} = kKC $$

When concentration is very low (i.e. $K_C \ll 1$), Eq. (1) simplifies to a pseudo-first-order kinetic law:

$$ \frac{dc}{dt} = k_1C $$

where $k_1$ is the pseudo-first-order rate constant. The rate constants, the linear plots of $-\ln(C/C_0)$ vs. time, shown in the inset of Fig. 2,
were calculated as 0.031 min\(^{-1}\), 0.043 min\(^{-1}\) and 0.031 min\(^{-1}\) for sulfachlorpyridazine, sulfapyridine and sulfisoxazole, respectively. So it can be seen that sulfachlorpyridazine and sulfisoxazole have the same degradation rates, while sulfapyridine degraded more quickly than the other two compounds.

3.2. Effect of the catalyst concentration

To optimize the TiO\(_2\) catalyst concentration, the effect of catalyst amount on the photocatalytic degradation rate of sulfa pharmaceuticals was carried out. Fig. 3 shows the dependence of TiO\(_2\) concentrations on the degradation rate constants. It was observed that all the rate constants increased with the increase of the amount of TiO\(_2\) catalyst for these three sulfa pharmaceuticals. The rate constants increased from 0.020, 0.029 and 0.027 min\(^{-1}\) at 0.25 g/L TiO\(_2\) to 0.032, 0.043 and 0.033 min\(^{-1}\) at 3.0 g/L TiO\(_2\) for sulfachlorpyridazine, sulfapyridine and sulfisoxazole, respectively. For sulfachlorpyridazine and sulfapyridine, the rate constants increased dramatically as TiO\(_2\) concentration is lower than 2.0 g/L, and then rose very slightly with further increase of catalyst concentration. While for sulfisoxazole, the rate constants increased linearly with TiO\(_2\) concentration ranged from 0.25 g/L to 3.0 g/L. These increases in the rate constants seem to be due to the increase in the total surface area of photocatalysts, namely number of active sites, available for the photocatalytic reaction as the dosage of photocatalyst increased [39]. These results suggest that the similar structures of these three sulfa pharmaceuticals have the similar change trends of degradation rates in the catalyst concentration range of 0.25–3.0 g/L.

3.3. Effect of the initial pH value

These three sulfa pharmaceuticals are all zwitter ionic compounds, generally existing as three different ionic forms in water, which mainly depend on the pH value of the solution. The first dissociation constants (pK\(_{a,1}\)) were measured to be 2.00 ± 3.00, 4.25 ± 0.30 and 1.50 ± 0.30, and the corresponding second dissociation constants (pK\(_{a,2}\)) were 5.90 ± 0.30, 8.43 ± 0.03 and 5.00 ± 0.07, for sulfachlorpyridazine, sulfapyridine and sulfisoxazole, respectively [17,18,40]. Thus the initial pH value can change the existed forms of sulfa pharmaceuticals in water, and thus significantly influence the photocatalytic degradation rates. Fig. 4 depicts the relationship between the rate constants with the initial pH values of three sulfa pharmaceuticals solution. From this figure, it can be seen that these three compounds have different change trends in the pH values range of 3.0–11.0. For sulfachlorpyridazine, the rate constant decreased very dramatically from 0.060 min\(^{-1}\) at pH value 3.0 to reach the bottom 0.031 min\(^{-1}\) at pH value 9.0, and then increased very slightly with the further increase of the pH value. While as for sulfapyridine, the curve of rate constants plot against pH value was much similar as that of the sulfachlorpyridazine. That is, the rate constants decreased at first from 0.049 min\(^{-1}\) at pH value 7.0, and then increased to 0.042 min\(^{-1}\) with further increasing the pH value up to 11.0. For sulfisoxazole, the curve of rate constants plot against pH value was almost linearly from 0.026 min\(^{-1}\) at pH value 3.0 to 0.052 min\(^{-1}\) at pH value 9.0, and then decrease to 0.050 min\(^{-1}\) at pH value 11.0. From the above results, it is found that the initial pH value has different influences on the photocatalytic degradation rate constants although these three sulfa pharmaceuticals have similar sulfanilamide structure. High rate constants in low pH value range for sulfachlorpyridazine (pK\(_{a,1}\) = 2 ± 3) and sulfisoxazole (pK\(_{a,1}\) = 1.5 ± 0.3) are because that they are difficult to be protonated in weak acidic solution (pH value ≥ 3.0), these neutral structure can be adsorbed onto the positively charged TiO\(_2\) surface below the zero point.
Fig. 5. The normalized sulfachlorpyridazine (a), sulfapyridine (b) and sulfisoxazole (c) concentration vs. adsorption time at various pH value with 100 μM and 2.0 g/L TiO₂ concentration.

However, the sulfapyridine (pKₐ,1 = 4.25 ± 0.3) is prone to be protonated in the same low pH value range, thus the electrostatic repulsion between the protonated sulfapyridine and the positive TiO₂ greatly retards their adsorption and subsequently results in the low photocatalytic degradation rate. On the other hand, with further increase of the pH value, sulfachlorpyridazine (pKₐ,2 = 5.90 ± 0.30) and sulfisoxazole (pKₐ,2 = 5.00 ± 0.07) will lose a proton and exist in anionic forms. Hence, these two negative sulfa pharmaceutical molecules cannot be easily adsorbed onto the surface of TiO₂ with the same negative charges (pH value ≥ 6.3). Nevertheless, sulfapyridine (pKₐ,2 = 8.43 ± 0.03) is a neutral molecule when the pH value is lower than 8.43 and thus the adsorption of sulfapyridine onto TiO₂ becomes much easier than the other two negative sulfa pharmaceuticals. Consequently, it is not surprised that low degradation rates for sulfachlorpyridazine and sulfisoxazole and high degradation rate for sulfapyridine were observed in weak alkaline solution as shown in Fig. 4.

In order to further validate the proposed conclusion that the photocatalytic degradation rate at the different pH values is significantly affected by the adsorption performance of sulfa pharmaceuticals onto TiO₂ surface, the adsorption kinetics of three sulfa pharmaceuticals was also carried out in detail. Fig. 5 shows the adsorption of sulfa pharmaceuticals against the adsorption time at various initial pH values. It was found that the acidic media were prone to the adsorption of sulfachlorpyridazine and sulfisoxazole onto TiO₂, while the adsorption of sulfapyridine was more efficient in neutral and alkaline media. These findings can be well confirmed by the conclusion that the photocatalytic degradation rates with different initial pH value were greatly controlled by the existed forms of the sulfa pharmaceuticals in the solution, which determined the adsorption amounts of sulfa pharmaceuticals onto TiO₂ in the solution.

3.4. Effect of the initial concentration

The dependence of the degradation rate constants on the initial concentrations of the substrate was also investigated and the results are shown in Fig. 6. It can be seen that the rate constants of all the three sulfa pharmaceuticals decrease with the increase of initial concentration, from 0.065, 0.095 and 0.056 min⁻¹ at 50 μM to 0.016, 0.020, and 0.018 min⁻¹ at 200 μM for sulfachlorpyridazine, sulfapyridine and sulfisoxazole, respectively. With 60 min illumination, all three sulfa pharmaceuticals with an initial concentration of 50 μM can be completely photocatalytically degraded, whereas at an initial concentration of 200 μM, only less than 70% of sulfa pharmaceuticals were destroyed (The data are not shown). Lower rate constants at higher initial concentration may be attributed to the fact that the more substrates can occupy more TiO₂ active sites, which subsequently suppress generation of the oxidants. Furthermore, the higher sulfa pharmaceutical concentrations absorb more photons, so the shortage of photons to activate TiO₂ inhibited the degradation of sulfa pharmaceuticals at a higher initial concentration [41].

Additionally, L–H equation also can be successfully used to describe the relationship between the photocatalytic degradation rate and the initial concentration of organic pollutant in heterogeneous photocatalytic degradation [36]. Through Eqs. (1) and (2), Eq. (3):

$$k_1 = \frac{kK}{1 + KC}$$

was obtained and transformed into its inverse function results in a linear relationship with an intercept of k⁻¹ and a slope k⁻¹KC⁻¹, as
According to Eq. (4) \[42,43\]:

\[
\frac{1}{k_1} = C \left( \frac{1}{k} + \frac{1}{KK} \right)
\]

where \( k_1 \) is the pseudo-first-order rate constant (min\(^{-1}\)), \( k \) is the intrinsic reaction rate constant (\( \mu M/min \)), and \( K \) is the \( L-H \) adsorption constant of sulfa pharmaceuticals over \( \text{TiO}_2 \) surface (\( \mu M^{-1} \)) in aqueous solution. Three satisfactory linear correlation coefficients were obtained as 0.994, 0.992, and 0.984 between 1/\( k_1 \) and the concentration of sulfa pharmaceuticals given in the insert of Fig. 6. From the slope, corresponding to 1/\( k \), and the y-intercept, corresponding to \( 1/KK \), the intrinsic reaction rate constant \( k \) got as 3.13, 3.72 and 4.07 \( \mu M/min \), and \( L-H \) adsorption constants \( K \) were also obtained as 2.40 \( \mu M^{-1} \), 1.02 \( \times 10^{-1} \mu M^{-1} \) and 3.56 \( \times 10^{-2} \mu M^{-1} \) for sulfachlorpyridazine, sulfapyridine and sulfisoxazole, respectively. It demonstrates that although the adsorption constants are at different order of magnitude, the intrinsic reaction rate constants are all at the same order of magnitude and with much closed values. A conclusion can be drawn that the degradation of all these three sulfa pharmaceuticals occurred mainly on the surface of \( \text{TiO}_2 \) by the oxidation reaction, such as photohole and \( \cdot \text{OH} \) radical, although their adsorption was so significantly different in neutral solution. Hence, the contribution of different ROSs to the photocatalytic degradation is needed to be further investigated.

### 3.5. The contribution of different ROSs

During photocatalytic degradation reaction, the generation of photoelectrons and photoholes pairs is the beginning of all the oxidation processes. Thus a series of ROSs, such as \( \cdot \text{OH}, \cdot \text{O}_2^-\), \( \cdot \text{HO}_2 \) and \( \text{H}_2\text{O}_2 \), are subsequently produced from primary active photogenerated holes and electrons [44]. In order to distinguish the contribution of the surface reaction with photohole or \( \cdot \text{OH} \) radical from other ROSs on the photocatalytic degradation of sulfa pharmaceuticals, different scavengers were employed to investigate their effects on the photocatalytic degradation kinetics. In this paper, 0.1 \( \mu M \) isopropanol was added in the reaction solution as scavengers of \( \cdot \text{OH} \) radicals [2], and potassium iodide (KI) was selected as scavengers of both \( \cdot \text{OH} \) radicals and photoholes [44,45]. It is because isopropanol can easily react with \( \cdot \text{OH} \) radicals converting into relatively inert isopropyl radical with a high bimolecular rate constant of 1.9 \( \times 10^{9} \text{M}^{-1} \text{S}^{-1} \) [2]. On the other hand, a commonly used electron donor, \( \text{I}^- \) ions, was selected to scavenge the photoholes and resulted \( \cdot \text{OH} \) radicals by forming relatively inert iodine radicals [44]. Thus the photocatalytic reaction can be partly suppressed with the addition of different scavengers in the reaction solution. The obtained pseudo-first-order rate constants with or without the addition of various scavengers and the corresponding regression coefficients are all presented in Table 1.

From Table 1, it was observed that the degradations of three sulfa pharmaceuticals were all suppressed in the presence of isopropanol. The pseudo-first-order rate constants decreased from 0.031, 0.043 and 0.031 min\(^{-1} \) to 0.010, 0.012 and 0.009 min\(^{-1} \) for sulfachlorpyridazine, sulfapyridine and sulfisoxazole, respectively. The degradation rate of these three sulfa pharmaceuticals with 67.7%, 72.1% and 71.0% is contributed by the \( \cdot \text{OH} \) radicals. Comparatively, the rate constants also decreased very significantly to 0.002 min\(^{-1} \), 0.004 min\(^{-1} \) and 0.003 min\(^{-1} \) after addition of KI scavengers in the reaction solution. These results indicated that 93.5%, 90.7% and 90.3% of the degradation rate of these three sulfa pharmaceuticals were originated from both the \( \cdot \text{OH} \) radicals and photoholes. Thus the contribution percentage of photoholes in the degradation rate was deduced as 25.8%, 18.6% and 19.3% by subtracting the percentage of \( \cdot \text{OH} \) radicals from the total percentage, for sulfachlorpyridazine, sulfapyridine and sulfisoxazole, respectively. Only 6.5%, 9.3% and 9.7% of the degradation rates were from other ROSs, for sulfachlorpyridazine, sulfapyridine and sulfisoxazole, respectively. Therefore, it can be concluded that the \( \cdot \text{OH} \) radicals are the predominant ROSs although both \( \cdot \text{OH} \) and \( \text{h}^+ \) together are responsible for the major degradation of sulfa pharmaceuticals. While the other ROSs (\( \text{H}_2\text{O}_2, \cdot \text{O}_2, \cdot \text{HO}_2 \) and \( \cdot \text{O}_2^- \)) together only play a very minor role in the degradation of three sulfa pharmaceuticals.

### 3.6. The preliminary reaction mechanism of sulfa pharmaceuticals

The disappearances of three selected sulfa pharmaceuticals as a function of the photocatalytic degradation time, together with evolution of decontaminated products, such as \( \text{NO}_3^-\), \( \text{NH}_4^+ \) and \( \text{SO}_4^{2-} \), are depicted in Fig. 7. After 60 min irradiation, 85.2%, 92.5% and 85.0% of sulfachlorpyridazine, sulfapyridine and sulfisoxazole are degraded, while 81.3%, 90.3% and 81.0% of sulfur atoms are converted into \( \text{SO}_4^{2-} \), respectively. These results indicated that the cracking of the \( \text{S}-\text{N} \) bond from sulfa pharmaceuticals was a main initial degradation pathway. In addition, the deamination of nitrogen atom is also found as an important pathway. However, for the conversion of nitrogen atom, the release of \( \text{NO}_3^- \) and \( \text{NH}_4^+ \) are significantly dependent on the structure of sulfa pharmaceuticals. As for sulfachlorpyridazine, only 17.2% nitrogen are released as \( \text{NO}_3^- \) (2.1%) and \( \text{NH}_4^+ \) (15.1%) in the solution, while the relative high conversion efficiencies of 70.5% (5.1% \( \text{NO}_3^- \) and 65.4% \( \text{NH}_4^+ \)) and 74.4% (5.1% \( \text{NO}_3^- \) and 69.4% \( \text{NH}_4^+ \)) are obtained for sulfapyridine and sulfisoxazole, respectively. Low conversion efficiencies of nitrogen atoms in sulfachlorpyridazine may be due to that the azo group in pyridazine ring is likely to be released as \( \text{N}_2 \) [46]. Ammonia ion is predominant specie of inorganic nitrogen released from degradation of all three sulfa pharmaceuticals. The percentages of \( \text{NH}_4^+ \) from the total inorganic nitrogen are obtained as 87.8%, 92.8% and 93.3% for sulfachlorpyridazine, sulfapyridine and sulfisoxazole, respectively. It is because that the nitrogen in heterocyclic aromatic rings can be transformed to both \( \text{NO}_3^- \) and \( \text{NH}_4^+ \) species, while secondary, tertiary and quaternary nitrogen atoms are photo-converted predominantly to ammonia [36]. From above-mentioned results, we can infer that all three sulfa pharmaceuticals can be partly photocatalytic decontaminated into harmless inorganic compounds via the production of a series of degraded intermediates. In order to further confirm this conclusion, TOC concentrations during the photocatalytic degradation of these three sulfa pharmaceuticals were measured, and the decrease profiles were also shown in Fig. 8. From the figure, it can be easily found that all these three pharmaceuticals can be almost mineralized into \( \text{CO}_2 \) with TOC decrease efficiencies of 90.8%, 88.8% and 81.5%, for sulfachlorpyridazine, sulfapyridine and sulfisoxazole, respectively.

Thus HPLC and HPLC/MS/MS were used to separate and identify the produced intermediates during the photocatalytic degradation. The structural assignments of all detected intermediates...
Fig. 7. The disappearance of sulfa pharmaceuticals and the evolution of nitrate, ammonium and sulphate ions during photocatalytic degradation of sulfachlorpyridazine (a), sulfapyridine (b) and sulfisoxazole (c) with 2.0 g/L TiO₂ and pH value 7.0.

Fig. 8. The decrease of TOC concentration for 100 μM sulfachlorpyridazine (■), sulfapyridine (▲) and sulfisoxazole (▲) with 2.0 g/L TiO₂ and pH value 7.0.

Fig. 9. The evolution of intermediates formed during the photocatalytic degradation of sulfachlorpyridazine (a), sulfisoxazole (b) and sulfapyridine (c) with 2.0 g/L TiO₂ and pH value 7.0 as a function of irradiation time.

The similar evolution profiles of the produced intermediates were obtained for three sulfa pharmaceuticals, and the detailed curves are shown in Fig. 9. From the figure, it can be seen that all intermediates were formed very fast, reached the maximum peak at 15 min or 20 min and then slowly disappeared. For sulfachlorpyridazine, three obtained earlier intermediates with \( m/z = 302 \) can be attributed to monohydroxylated intermediates. At the same time, two daughter intermediates with \( m/z = 318 \) were also detected, which are corresponding to dihydroxylated derivatives of sulfachlorpyridazine. One more identified intermediate with \( m/z = 130 \) can be assigned to 6-chloropyridazin-3-amine, which was produced from the cleavage of S–N bond. Its corresponding further oxidative intermediate with \( m/z = 112 \) was also detected (shown in Fig. 9a). As for sulfisoxazole, the similar degradation intermediates were also found (shown in Fig. 9b). Similar to sulfachlorpyridazine, two monohydroxylated intermediates with \( m/z = 284 \) and two dihydroxylated intermediates with \( m/z = 300 \) were also found. The intermediate with \( m/z = 114 \) was also detected (shown in Fig. 9b).
and lost sulfaniline, and its corresponding further oxidative intermediate with \( m/z = 113 \), 3, 4-dimethylisoxazol-5-ol, were also found. For sulfonylpyridine (shown in Fig. 9c), two monohydroxylated intermediates with \( m/z = 266 \) were identified, while the dihydroxylated intermediates were not detected. The daughter intermediate with \( m/z = 95 \), 2-amine-pyridin, originated from the cleavage of S–N bond and lost sulfaniline, was also found for this compound.

By comparison of the intermediates produced during the photocatalytic degradation of three sulfa pharmaceuticals and consideration of the predominant contribution of \( \bullet OH \) radicals and photoholes from above results, two main common initial photocatalytic degradation pathways for all three sulfa pharmaceuticals were proposed as illustrated in Fig. 10. The hydroxylation addition was considered as the predominant degradation route. It is because the earlier monohydroxylated intermediates with \( m/z = 302, 284 \) and 266 were all detected for sulfonylpyridazine, sulfoxazole and sulfapyridine, respectively. And the daughter dihydroxylated intermediates with \( m/z = 318 \) and 300 were also found for sulfonylpyridazine and sulfoxazole, respectively. On the other hand, the cracking of S–N bond attacked by \( h^+ \) was also found as a secondary importance degradation route. Although the corresponding moiety of 4-aminobenzenesulfonic acid was not found, the intermediates of RNH\(_2\) produced by the cracking of S–N bond were all evidently detected during the photocatalytic degradation process of these three sulfa pharmaceuticals (shown in Fig. 10).

4. Conclusion

The photocatalytic degradation kinetics of three sulfa pharmaceuticals in aqueous solution was investigated in detail and the conclusion was drawn that three sulfa pharmaceuticals can be degraded efficiently with a removal efficiencies of 85.2%, 92.5% and 85.0% after 60 min illumination. Various influence parameters on kinetics were also investigated. The results indicated that the degradation rates increase with the increase of catalyst dosage, while the initial pH value can significantly influence the adsorption and subsequently affect the degradation of different sulfa pharmaceuticals and then result in different change trends of degradation rates in the pH value range of 3.0–11.0. As for the effect of the initial concentration of sulfa pharmaceuticals, the degradation rates decrease with the increasing of substrate concentration. The dependence of the photocatalytic degradation rate on the initial concentration of sulfa pharmaceuticals suggested that the oxidation reaction occurred on the surface of TiO\(_2\) played an important role in the degradation of these three sulfa pharmaceuticals. The further study on the contribution of the ROSs indicates that both \( h^+ \) and particular \( \bullet OH \) together are responsible for the major degradation of all these three sulfa pharmaceuticals, the other ROSs play a minor role during this process. For all sulfa pharmaceuticals examined, more than 81.0% of the sulphurs are photo-converted into \( SO_4^{2-} \), and the nitrogens are converted predominantly into NH\(_4^+\) and a less extent into NO\(_3^-\). It must be note that, for sulfonylpyridazine, only a very small percentage of NH\(_4^+\) was produced as compared with the other two compounds. Variations in these products during the transformation of sulfa pharmaceuticals are dependent on the substrates molecular structure. At last, a general photocatalytic degradation mechanism was tentatively proposed, and the hydroxylation addition reaction and the cracking of S–N bond resulted by photohole are considered as two predominant routes for the degradation of sulfa pharmaceuticals.

Acknowledgments

This is contribution No. IS-1172 from GIGCAS. The authors appreciate the financial supports from National Nature Science Foundation of China (No. 40973068), the Earmarked Fund of the State Key Laboratory of Organic Geochemistry (SKLOG2009A02) and Knowledge Innovation Program of Chinese Academy of Sciences (No. KZZX2-YW-QN103).

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Fig. 10. The proposed pathways of photocatalytic degradation of sulfa pharmaceuticals.