

## Degradation of acid red 14 by silver ion-catalyzed peroxydisulfate oxidation in an aqueous solution

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### Abstract

Silver ion ( $\text{Ag}^{1+}$ )-catalyzed peroxydisulfate was studied for the degradation of acid red 14 (AR-14) in an aqueous medium. The effect of different parameters, such as temperature, peroxydisulfate concentration, and dye and  $\text{Ag}^{1+}$  concentrations, were investigated.

Application of  $\text{Ag}^{1+}$ -catalyzed peroxydisulfate, as an advanced oxidation process, introduces an effectual method for wastewater treatment. An accelerated reaction using  $\text{S}_2\text{O}_8^{2-}$  to destroy dyes can be achieved via chemical activation with  $\text{Ag}^{1+}$  to generate sulfate radicals ( $\text{SO}_4^-$ ). Degradation efficiency was not considerable when using peroxydisulfate alone. Studies revealed that increases in temperature and in the initial concentrations of peroxydisulfate and  $\text{Ag}^{1+}$  up to 80 mM and 10 mM, respectively, enhanced dye degradation, while a decrease in the initial dye concentration would also enhance the efficiency of its degradation.

**Key Words:** Advanced oxidation process, peroxydisulfate, acid red 14,  $\text{Ag}^{1+}$  catalyst, wastewater treatment

### 1. Introduction

The textile industry produces large amounts of highly colored effluents, which are generally toxic and resistant to destruction by biological treatment methods. Azo dyes, such as acid red 14 (AR-14), are widely used in the textile industry (Lachheb et al., 2002; Daneshvar et al., 2003). Various chemical and physical processes, such as chemical precipitation and separation of pollutants, coagulation, electrocoagulation, or elimination by adsorption on activated carbon, are applied for color removal from textile effluents (Daneshvar et al., 2004).

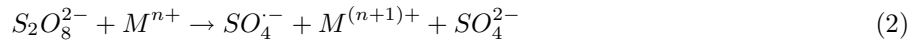
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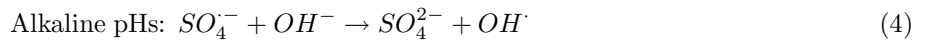
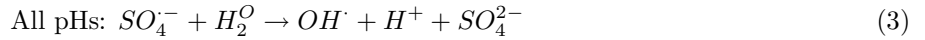
In the last decades, chemical oxidation of contaminants in the natural environment by oxidants has been studied to develop novel remediation technologies. The oxidants  $\text{H}_2\text{O}_2$ ,  $\text{KMnO}_4$ ,  $\text{O}_3$ , Fenton's reagent, and peroxydisulfate ( $\text{S}_2\text{O}_8^{2-}$ ) have been widely tested in laboratory work and field applications and used for the remediation of soil and groundwater contaminated by organic compounds. The use of peroxydisulfate has recently been the focus of attention for an alternative oxidant in the chemical oxidation of contaminants (Huang et al., 2005; Oh et al., 2009). Peroxydisulfate is relatively stable at room temperature; it is a strong oxidizing agent ( $E^0 = 2.01 \text{ V}$ ) and nonselective. It also promotes  $\text{H}_2\text{O}_2$  for the following reasons as a reagent in the oxidative process: 1) Peroxydisulfate ions seem to be more promising because of the potential quenching effect of using  $\text{H}_2\text{O}_2$  when the process is not well controlled (such as overdosing). 2) Peroxydisulfate is much cheaper than other oxidants like hydrogen peroxide and ozone. 3) Since peroxydisulfate is a solid oxidant, it would be more suitable for industrial uses in comparison to liquid oxidants such as  $\text{H}_2\text{O}_2$  and  $\text{KMnO}_4$ .

The ion of  $\text{S}_2\text{O}_8^{2-}$  has great capability for degrading numerous organic contaminants through free radicals (e.g.,  $\text{SO}_4^-$  and  $\text{OH}$ ) generated in the peroxydisulfate system (Couttenye et al., 2002; Huang et al., 2005; Oh et al., 2009).

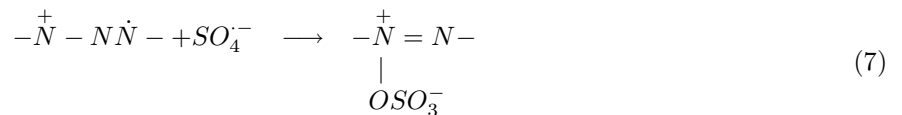
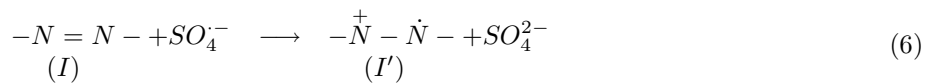
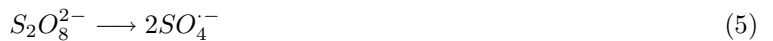
Heat, transition metal ions ( $\text{M}^{n+}$ ), and UV light can excite  $\text{S}_2\text{O}_8^{2-}$  to form a sulfate radical ( $\text{SO}_4^-$ ), a stronger oxidant ( $E^0 = 2.60 \text{ V}$ ) than  $\text{S}_2\text{O}_8^{2-}$ , to significantly enhance the oxidation of contaminants, as shown in Eqs. (1) and (2).

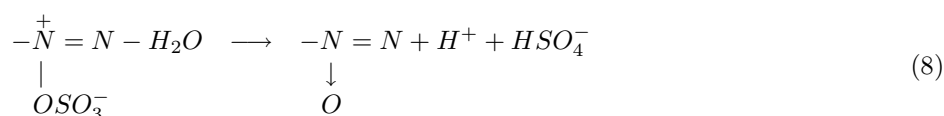


Hydroxyl radicals can also be formed via Eqs. (3) and (4) in the peroxydisulfate-water system. Both  $\text{SO}_4^-$  and  $\text{OH}$  are possibly responsible for the destruction of organic contaminants.

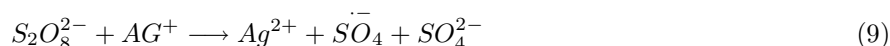


Sulfate radicals ( $\text{SO}_4^-$ ) and hydroxyl radicals ( $\text{OH}$ ) are generated as a result of the heat decomposition of  $\text{S}_2\text{O}_8^{2-}$  in aqueous phases. Using electron paramagnetic resonance techniques, Couttenye et al. (2002) reported that, in neutral to acidic solutions (pH 2-7), the formation of  $\text{SO}_4^-$  is observed, and in solutions with pH levels above 12,  $\text{OH}$  is the active species formed in  $\text{S}_2\text{O}_8^{2-}$  systems. In order to study the effect of  $\text{Ag}^{1+}$ -catalyzed and uncatalyzed oxidative decolorization of AR-14 as an azo dye by the peroxydisulfate system, the following mechanism was proposed (Gemeay et al., 2007) for the uncatalyzed oxidation process of azo dyes.



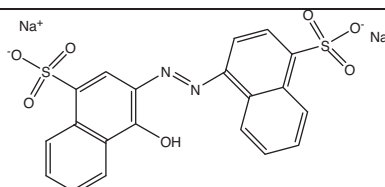


The formation of the azoxy product in Eq. (8) was previously reported for the oxidation of azo-containing compounds such as 4-(phenylazo)diphenylamine and some direct dyes (Salem et al., 1995; El-Daly et al., 2005).  $-N=N(I)$  and  $-N^+-N(I')$  are referred to as the azo center of the compounds and their radical intermediate species, respectively. The oxidation reaction of AR-14 is very slow in the absence of a catalyst.  $Ag^{1+}$  was chosen as a catalytic species to accelerate the reaction rate.



In the oxidation process, sulfate ions will be generated as the end product, which leads to an increase in salt content in the effluent. The  $S_2O_8^{2-}$  is practically inert and is not considered to be a pollutant. In the present study, the oxidation of AR-14 (Table) via  $Ag^{1+}$ -activated peroxydisulfate was investigated in a batch system.

**Table.** Properties of AR-14.

Colour Index	Acid red 14
Azo groups	1
Type	Anionic
Structure	
$\lambda_{max}$ (nm)	514
Molecular weight (g/mol)	502.4

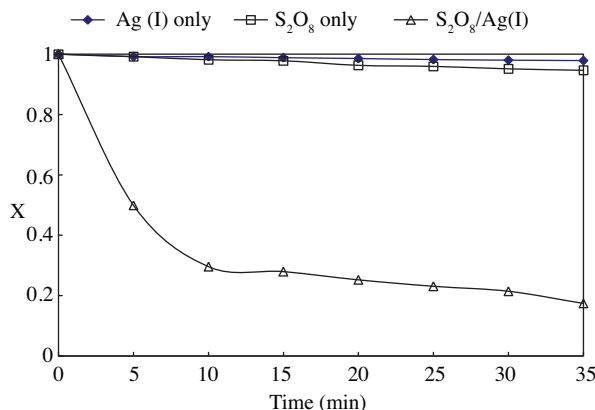
## 2. Materials and methods

The dye AR-14 was provided by Sigma-Aldrich and used without further purification. Silver nitrate was obtained from AppliChem and ammonium peroxydisulfate from Merck. The solution was immediately prepared before the measurements to avoid a change in concentration due to self-decomposition. Other chemicals were of analytical reagent grade and were used without further purification.

Experiments were carried out in a batch reactor. The scheme of the experimental set-up is shown in Figure 1. Added to the dye-and- $Ag^{1+}$  solution in a glass bottle was 50 mL of synthetic solution containing the desired initial concentration of  $S_2O_8^{2-}$ ; this was mixed using a magnetic stirrer. The dye solution samples were taken at the desired time intervals and were analyzed with a UV/Vis spectrophotometer (Shimadzu UV-160) at  $\lambda_{max} = 514$  nm with a calibration curve based on the Beer-Lambert law. The operating conditions of all experimental test runs are summarized in the captions of Figures 2-7. The efficiency of color removal was

expressed as the ratio of  $C_t$  to  $C_0$ , as in Eq. (10), where  $C_0$  is the initial concentration value of AR-14 and  $C_t$  is the concentration value of AR-14 at time  $t$ .

$$X = \frac{C_t}{C_0} \quad (10)$$



**Figure 2.** Effect of  $S_2O_8^{2-}/Ag^{1+}$  process in oxidative decolorization of AR-14.  $[AR-14]_0 = 0.04$  mM,  $[S_2O_8^{2-}]_0 = 80$  mM,  $[Ag^+]_0 = 0.2$  mM,  $pH_0 = \text{natural (5.8)}$ ,  $T = 25$  °C.

### 3. Results and discussion

#### 3.1. Effect of $S_2O_8^{2-}$ and $Ag^{1+}$ on degradation of AR-14

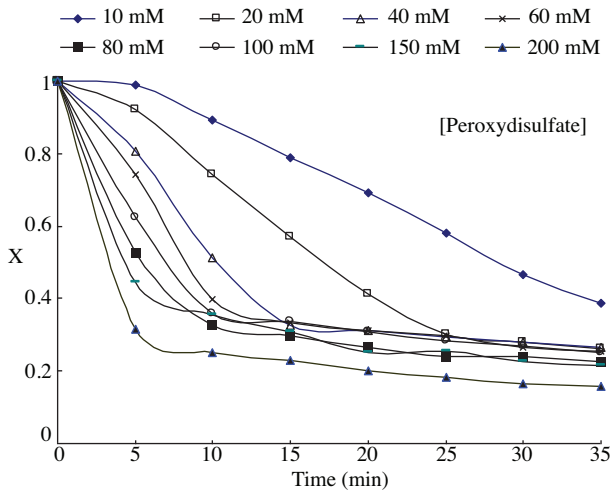
The degradation of AR-14 was investigated using  $S_2O_8^{2-}$  alone,  $Ag^{1+}$  without peroxydisulfate, and both  $Ag^{1+}$  and  $S_2O_8^{2-}$ . There was no observable loss of color when  $S_2O_8^{2-}$  was applied in the absence of  $Ag^{1+}$ , and the color removal was not considerable when using  $Ag^{1+}$  in the absence of  $S_2O_8^{2-}$ . The results reveal that a considerable decrease in the concentration of the dye occurred when the sample was oxidized by  $S_2O_8^{2-}$  in the presence of the  $Ag^{1+}$  catalyst because of sulfate radicals generated due to the chemical activation of peroxydisulfate with  $Ag^{1+}$ .

#### 3.2. Effect of initial peroxydisulfate concentration

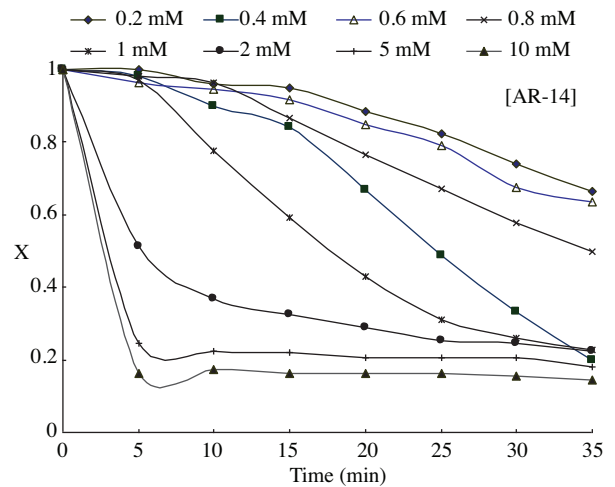
The concentration of  $S_2O_8^{2-}$  was found to be an important parameter for the degradation of AR-14 by  $S_2O_8^{2-}$  oxidation. The decay of AR-14 is indicated in Figure 3 for different initial peroxydisulfate concentrations of 5, 10, 20, 40, 80, 100, 150, and 200 mM, with initial AR-14 and  $Ag^{1+}$  concentrations of 0.04 and 0.2 mM, respectively, at room temperature (25 °C). This is likely because sulfate radicals were generated simultaneously and improved the oxidative decolorization of AR-14. Furthermore, when the  $S_2O_8^{2-}$  concentration increased beyond 80 mM, the increment of the AR-14 decay rate slowed down slightly. The excess radicals generated may undergo recombination or may become involved in the side reactions, which is implied by the overlap of the curves in Figure 3. Oxidizing species (mostly likely  $SO_4^-$  under the experimental conditions) might dominate the reaction with AR-14, although numerous oxidizing species, such as  $SO_4^-$ , OH and  $S_2O_8^{2-}$ , could exist in the system and react with the dye (Li et al., 2009; Salari et al., 2009).

### 3.3. Effect of the initial $\text{Ag}^{1+}$ concentration

Degradation of the AR-14 (0.04 mM) was investigated using different concentrations of  $\text{Ag}^{1+}$  and 80 mM  $\text{S}_2\text{O}_8^{2-}$  at the initial natural pH of 5.8 and a room temperature of 25 °C. Figure 4 shows the effect of the initial  $\text{Ag}^{1+}$  concentration on the decolorization efficiency. It can be seen that the removal efficiency increased as the initial  $\text{Ag}^{1+}$  concentration was increased with the same concentration of  $\text{S}_2\text{O}_8^{2-}$ . This observation may be explained by the fact that increasing the  $\text{Ag}^{1+}$  concentration according to Eq. (9) accelerated the conversion of  $\text{S}_2\text{O}_8^{2-}$  to  $\text{SO}_4^-$  to oxidize AR-14 rapidly (Anipsitakis et al., 2004).



**Figure 3.** Effect of initial concentration of  $\text{S}_2\text{O}_8^{2-}$  in oxidative decolorization of AR-14.  $[\text{S}_2\text{O}_8^{2-}]_0 = 5, 10, 20, 40, 80, 100, 150,$  and  $200$  mM;  $[\text{AR-14}]_0 = 0.04$  mM;  $[\text{Ag}^+]_0 = 0.2$  mM;  $\text{pH}_0 = \text{natural (5.8)}$ ;  $T = 25$  °C.



**Figure 4.** Effect of initial concentration of  $\text{Ag}^+$  in oxidative decolorization of AR-14.  $[\text{Ag}^+]_0 = 0.2, 0.4, 0.6, 0.8, 1, 2, 5,$  and  $10$  mM;  $[\text{AR-14}]_0 = 0.04$  mM;  $[\text{S}_2\text{O}_8^{2-}]_0 = 80$  mM;  $\text{pH}_0 = \text{natural (5.8)}$ ;  $T = 25$  °C.

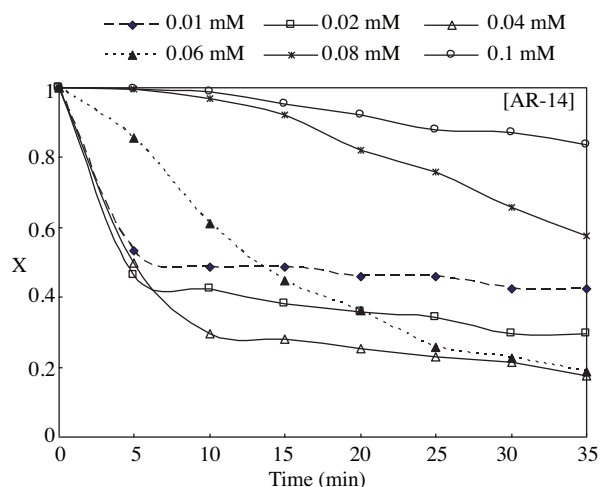
### 3.4. Effect of initial dye concentration

It is important from an application point of view to study the dependence of removal efficiency on the initial concentration of dye. The results in Figure 5 show the dye degradation with 80 mM  $\text{S}_2\text{O}_8^{2-}$  and 0.2 mM  $\text{Ag}^{1+}$  at an initial natural pH (5.8) and room temperature (25 °C). It was observed that the dye removal increased rapidly at low AR-14 concentrations and then changed slowly as the initial concentration increased at a fixed concentration of  $\text{S}_2\text{O}_8^{2-}$  (Modirshahla et al., 2006).

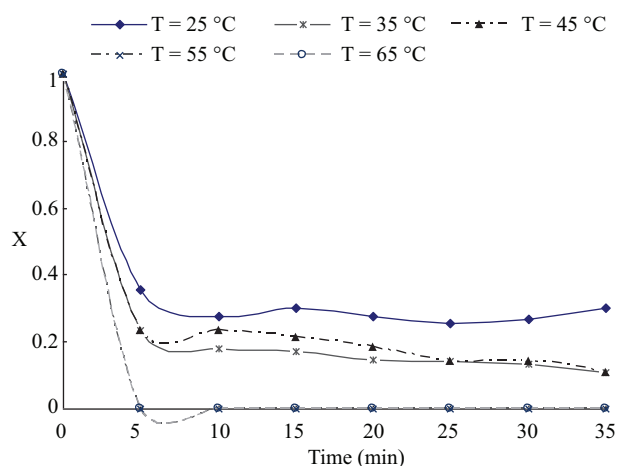
### 3.5. Effect of temperature

The results in Figure 6 show that the percentage of AR-14 degradation after 35 min at 25, 35, 45, 55, and 65 °C illustrates the effect of temperature on the reactions of peroxydisulfate with AR-14. Comparison of the data reveals that the reaction rates increased with increasing reaction temperature. In addition, the activation energy of the degradation reaction could be obtained based on the experimental data using the Arrhenius equation,  $k = A\exp(-E_a/RT)$ , where  $A$  is the frequency factor,  $E_a$  is the activation energy,  $R$  is the universal

gas constant, and  $T$  is the temperature in Kelvin, indicating that heat energy can activate peroxydisulfate to sulfate radicals more effectively (Couttenye et al., 2002; Huang et al., 2005).



**Figure 5.** Effect of initial dye concentration in oxidative decolorization of AR-14.  $[AR-14]_0 = 0.01, 0.02, 0.04, 0.06, 0.08,$  and  $0.1$  mM;  $[S_2O_8^{2-}]_0 = 80$  mM;  $[Ag^+]_0 = 0.2$  mM;  $pH_0 =$  natural (5.8);  $T = 25$  °C.



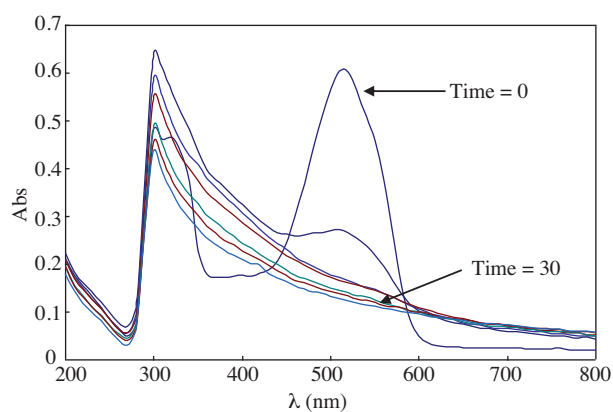
**Figure 6.** Effect of temperature in oxidative decolorization of AR-14.  $T = 25, 35, 45, 55,$  and  $65$  °C;  $[S_2O_8^{2-}]_0 = 80$  mM;  $[Ag^+]_0 = 0.2$  mM;  $[AR14]_0 = 0.04$  mM;  $pH_0 =$  natural (5.8).

### 3.6. Spectral changes of AR-14 during oxidation by peroxydisulfate

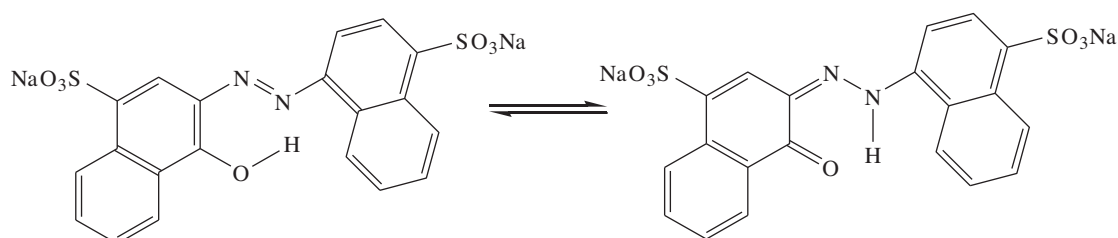
The color of an azo dye is the result of the interaction between an azo function ( $-N=N-$ ) and 2 aromatic species: the dyes carry an acceptor group, which is an aromatic nucleus frequently containing a chromophoric group such as  $-SO_3^-$ , and a donor group, e.g., an aromatic nucleus containing an auxochromic group such as an OH group (Galindo et al., 2001). The changes in the absorption spectra of AR-14 solutions (0.04 mM) during the oxidation process in 80 mM  $S_2O_8^{2-}$  and 0.2 mM  $Ag^{1+}$  at an initial natural pH (5.8) and room temperature (25 °C) at different times are shown in Figure 7. The decrease of the absorption peak of the dye at  $\lambda_{max} = 514$  nm indicates a rapid degradation of the azo dye. The decrease is also meaningful with respect to the nitrogen-to-nitrogen double bond ( $-N=N-$ ) of the azo dye as the most active site for oxidative attack. The decrease in the absorption intensity of the band at  $\lambda_{max}$  during the oxidation also expresses the loss of conjugation; in particular, the cleavage nears the azo bond of the organic molecule. The weak band at 310-330 nm could be attributed to the  $\pi-\pi^*$  transition related to the aromatic ring attached to the  $-N=N-$  group in the dye molecule. The absorbance decrease at 310-330 nm indicates the degradation of the aromatic part of the dye.

### 3.7. Effect of $S_2O_8^{2-}$ and $Ag^{1+}$ on degradation of AR-14

The degradation pathway of AR-14 could be explained as follows: the fragile group in this dye is the NH group, which results from an equilibrium between 2 tautomeric forms, where an H atom is exchanged between O and N, as shown in Figure 8. Indeed, the abstraction of the H atom (carried by an oxygen atom in the azo form and by a nitrogen atom in the hydrazone form) by sulfate or hydroxyl radicals is the main degradation pathway of this dye (Khataee et al., 2009).



**Figure 7.** Spectral changes of AR-14 solution during illumination in the presence of  $S_2O_8^{2-}$  and  $Ag^{1+}$ .  $[S_2O_8^{2-}]_0 = 80$  mM,  $[Ag^{1+}]_0 = 0.2$  mM,  $[AR-14]_0 = 0.04$  mM,  $pH_0 = \text{natural (5.8)}$ ,  $T = 25$  °C.



**Figure 8.** Equilibrium between the 2 tautomeric forms in AR-14.

#### 4. Conclusion

Application of peroxydisulfate along with  $Ag^{1+}$  introduces an effectual and safe method for oxidative removal of AR-14 at the laboratory scale. The degradation rate of AR-14 was shown to be dependent on the temperature and the  $Ag^{1+}$ , dye, and peroxydisulfate concentrations. The higher the concentration of dye was, the lower the decolorization percentage was. An increase in peroxydisulfate concentration, meanwhile, enhanced the degree of degradation. The results indicate that degrees of degradation of AR-14 were obviously increased by increasing the initial concentration of  $Ag^{1+}$ .

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