

Degradation of Acid Orange 7 in a persulfate-bisulfite system under visible light

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Textile industry is one of the most significant manufacturing sectors that produce large volumes of highly polluted and toxic wastewater. Dyes represent an important part of waste effluents. In this study, the degradation of Acid Orange 7 dye (AO7) in a persulfate-bisulfite (PS-BS) system under visible (Vis) light (wavelength more than 420 nm) was performed. All batch experiments were conducted in a 100 mL undivided glass beaker containing 50 mL solution at about 25 °C without irradiation or under irradiation by a direct exposure visible light power supply (CHF-XM-500W) from Beijing Trusttech Co. (China). After the desired amounts of AO7 and PS in 50 mL of the aqueous solution were added into the reactor, the reaction was initialized by adding BS. To monitor the degradation process of AO7, solution samples were taken out at given reaction time intervals and measured immediately on a METASH UV-5500PC spectrophotometer under the maximum absorption wavelength (484 nm) to record the temporal UV-vis spectral variations of the dye. The related reaction progress was monitored using the UV-vis absorption spectra of AO7 in terms of the percentage of degraded azo-dye. The activities of different systems including BS/Vis, PS/BS, PS/Vis and BS/PS/Vis were evaluated. It was found that the efficiency of PS/Vis system was negligible, and almost 29 and 40% of AO7 was oxidized by BS/Vis and BS/PS within 30 min, and it was further improved to almost 94% within 30 min by BS/PS/Vis system at room temperature. Various operational parameters, such as PS concentration, BS concentration and initial pH were investigated to optimize the process.

Keywords: Dye's degradation, Acid Orange 7, Bisulfite, Persulfate, Visible light, Inorganic negative ions.

Industrialization plays an important role in the development of the society, but it has led to severe environmental pollution. Dyes represent an important part of waste effluents, as they are discharged in abundance by many manufacturing industries. It is recorded that more than 100,000 commercially available textile dyes are present in the market and approximately 700000–1000000 tons of dyes are produced while 280000 tons are discharged via effluents generated from the textile industry to the global environment annually. Thus, textile industry is one of the most significant manufacturing sectors that produce large volumes of highly polluted and toxic wastewater. According to the World Bank estimates, the textile industry is the source of 17 to 20% of industrial pollution of water, which is highly colored with a significant amount of dyes. Because of toxicity, non-biodegradability and potential carcinogenicity, the discharge of colored wastewater without proper and adequate treatment negatively affects the aquatic biota and ecosystems.

A number of articles have appeared on the persulfate-bisulfite redox system, used industrially as a redox initiation system, during which free radicals, such as hydroxyl radical (OH•) and sul-

fate radical $\text{SO}_4^{\cdot-}$ generated [1–6]. As the powerful oxidants, OH• with a redox potential of 1.8–2.7 V vs. NHE (normal hydrogen electrode), and $\text{SO}_4^{\cdot-}$ with the same or even a higher redox potential of 2.5–3.1 V vs. NHE could degrade the organic contaminants efficiently [7, 8]. However, as per the literature, little is reported about the application of the persulfate-bisulfite couple to degrade organic compounds until now. To obtain some information about the degradation of organic pollutants by the persulfate-bisulfite couple, as a representative compound of azo dyes, AO7 was selected for this study. To further improve the efficiency of the persulfate-bisulfite couple, visible (Vis) light was introduced.

Experimental

Materials

Acid Orange 7 (AO7, $\text{C}_{16}\text{H}_{11}\text{N}_2\text{NaO}_4\text{S}$) was purchased from Aladdin Industrial Corporation. Sodium hydrogen sulfite (NaHSO_3), sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) and other chemicals were of analytical grade if not noticed otherwise and were obtained from Sinopharm Chemical Reagent Co., Ltd. Acetonitrile was also purchased from

Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) but with HPLC grade. All chemicals were used as received without further purification. The sample solutions were prepared using deionized water (Aquapro, USA) throughout the experiments.

Degradation procedures

All batch experiments were conducted in a 100 mL undivided glass beaker containing 50 mL solution at about 25 °C without irradiation or under irradiation by a direct exposure Vis light power supply (CHF-XM-500W) from Beijing Trusttech Co. (China). After the desired amounts of AO7 and PS in 50 mL of the aqueous solution were added into the reactor, the reaction was initialized by adding HSO_3^- . Each reaction solution was constantly agitated by a magnetic stirrer (model 78-1, Hangzhou Instrument Motors Factory, China).

A stock solution of AO7 with the initial concentration (C_0) 20 mg/L was prepared freshly with deionized water before each run. Since PS is an acidic oxidant, the addition of PS led to a significant decrease of pH, and the experiment was conducted at acidic medium (pH 4.75, no adjustment). For studying the effect of solution pH on the rate of AO7 degradation, 0.1 M sulfuric acid (Pronolab, 98%, 1.84 g/cm³) and 0.1 M sodium hydroxide (Quimitécnica, 30% w/v, 1.33 g/cm³) were used to adjust the solution pH after PS was added into the solution. Before the beginning of reaction, PS solution and HSO_3^- solution were added to the reactor.

Analysis

To monitor the degradation process of AO7, solution samples were taken out at given reaction time intervals and measured immediately on a METASH UV-5500PC spectrophotometer under the maximum absorption wavelength (484 nm) to record the temporal UV-vis spectral variations of the dye. The related reaction progress was monitored using the UV-vis absorption spectra of AO7 in terms of the percentage of degraded azo-dye, which was calculated from the following equation (1):

$$\begin{aligned} \text{Decolorization efficiency (\%)} = \\ = (C_0 - C_t) / C_0 \cdot 100, \end{aligned} \quad (1)$$

where C_t is the absorbance at 484 nm for AO7 at a given reaction time t and C_0 is the related initial absorbance.

Results and discussion

Degradation efficiency of AO7 under different systems

To evaluate the activities of different systems, 20 mg/L AO7 was treated for 30 min by HSO_3^- /

PS process, PS/Vis process, HSO_3^- /Vis process and HSO_3^- /PS/Vis process. As shown in Figure 1 (see color insert), negligible removal was observed when AO7 was treated by PS/Vis; $\approx 29\%$ and $\approx 40\%$ of AO7 was oxidized by HSO_3^- /Vis and HSO_3^- /PS within 30 min respectively, while the oxidation efficiency was significantly improved under vis light: $\approx 94\%$ of AO7 was oxidized within 30 min. PS is relatively stable at ambient temperature and could hardly degrade AO7 via direct photolysis, as its oxidation potential was very limited ($E^0 = 2.01$ V vs. NHE) [9]. However, AO7 could be degraded by HSO_3^- /PS, and the efficiency of the system HSO_3^- /PS/Vis was much higher than that of HSO_3^- /PS.

Spectral change of AO7

AO7 degradation was monitored in the experimental runs by means of UV/Vis scanning of the whole range of wavelengths available for a diode array and UV/Vis spectra were recorded at different time intervals in Figure 2 (see color insert). As can be seen, the representative radiation absorption spectrum of the dye solution is characterized by the band in the Vis region, with the maxima located at 484 nm, corresponding to the $n-\pi^*$ transition of the azo chromophore ($-\text{N}=\text{N}-$), which accounts for the orange color of solution, and by two bands in the ultraviolet region located at 228 nm and 310 nm, considered to be associated with the $\pi-\pi^*$ transition in the benzene and naphthalene rings, respectively [10, 11].

It is observed that the intensity of the signal at 484 nm obviously decreased with the reaction time and finally to disappear, indicating the destruction of azo chromophore. At the meantime, the decrease of the bands at 228 and 310 nm in ultraviolet region was observed, due to the fragmentation of aromatic structures in the dye molecule and its intermediates [12–14].

In addition, the absorbance at 206 nm remarkably increased from 1.1846 to 1.4108 during the first 2.5 min, and then decreased to 1.3118 after 30 min. It could be speculated that colorless intermediates were produced and accumulated during the decolorization process, and then some of them were further degraded during the extended degradation period.

Effect of PS concentration

Different amounts of PS were used to investigate the effect of PS dosage on AO7 oxidation. Figure 3 (see color insert) illustrates the removal efficiency of AO7 at different PS concentrations with initial AO7 concentration 20 mg/L, HSO_3^- concentration 0.2 mM, initial

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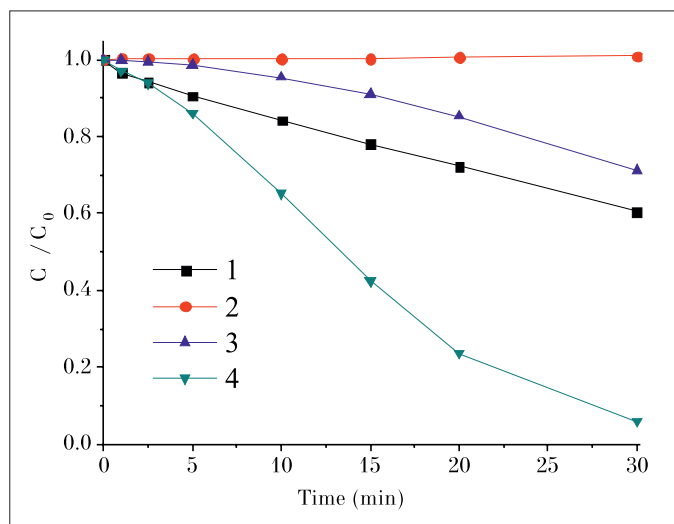


Fig. 1. Degradation of AO7 in different systems:
PS/HSO₃⁻ (1), PS/Vis (2),
HSO₃⁻/Vis (3), PS/HSO₃⁻/Vis (4)

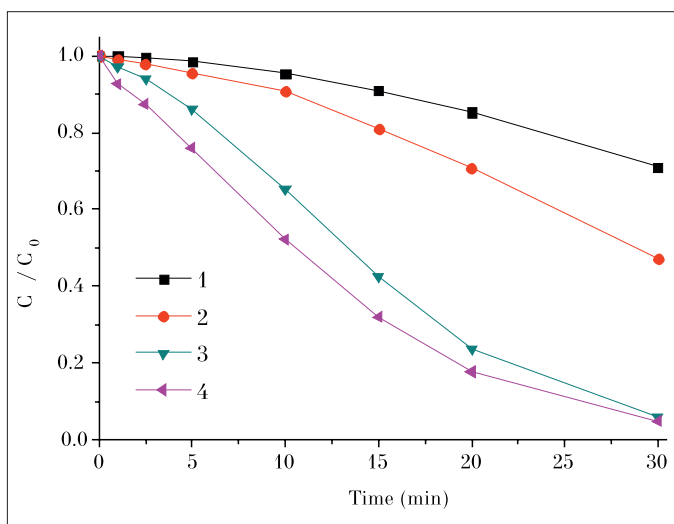


Fig. 3. The effect of PS concentration (g/L):
(1) 0, (2) 0.05, (3) 0.2, (4) 0.4.

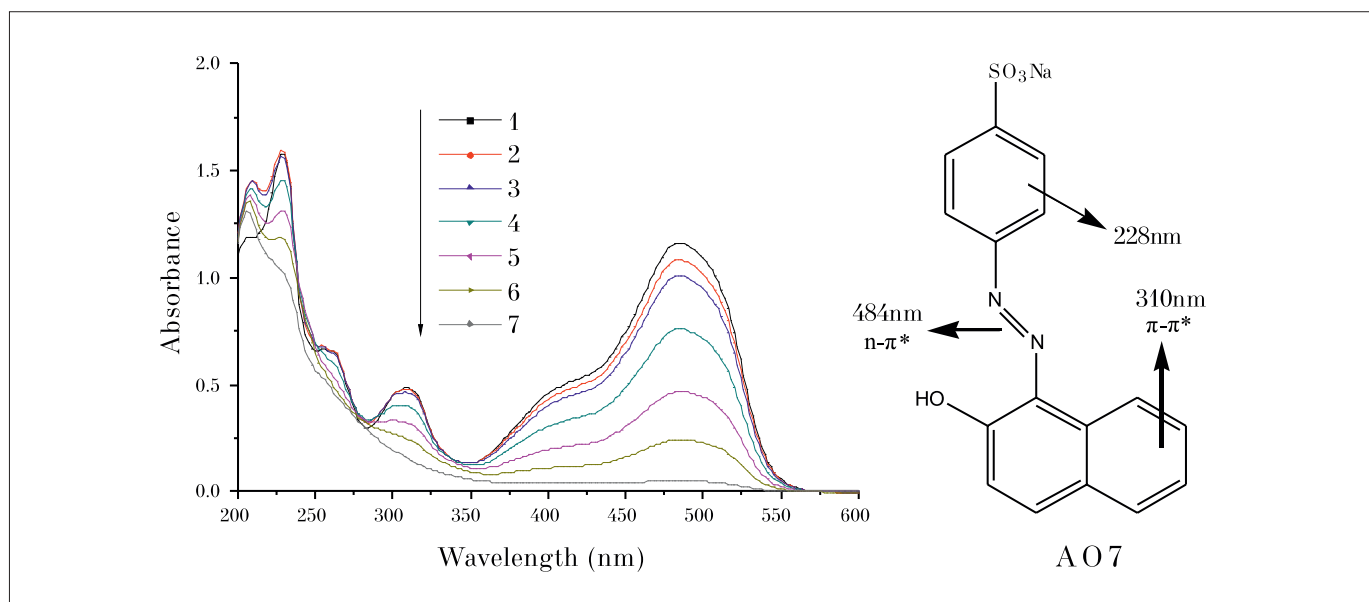


Fig. 2. UV/Vis light absorption spectrum decreasing for AO7 by Vis/HSO₃⁻/PS process (left-side) at different time (min): (1) 0, (2) 2.5, (3) 5, (4) 10, (5) 15, (6) 20, (7) 30. And the chemical structure of AO7 with assignments for the absorption maximum peaks (right-side)

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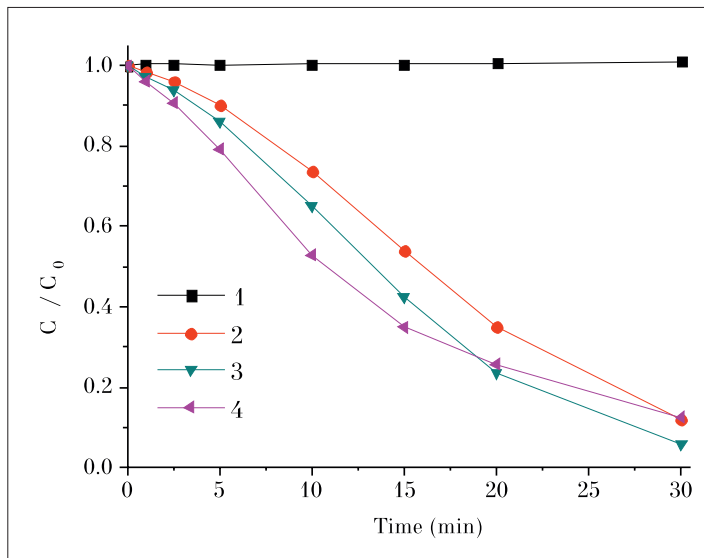


Fig. 4. The effect of HSO_3^- concentration (mM): (1) 0, (2) 0.5, (3) 2, (4) 4.

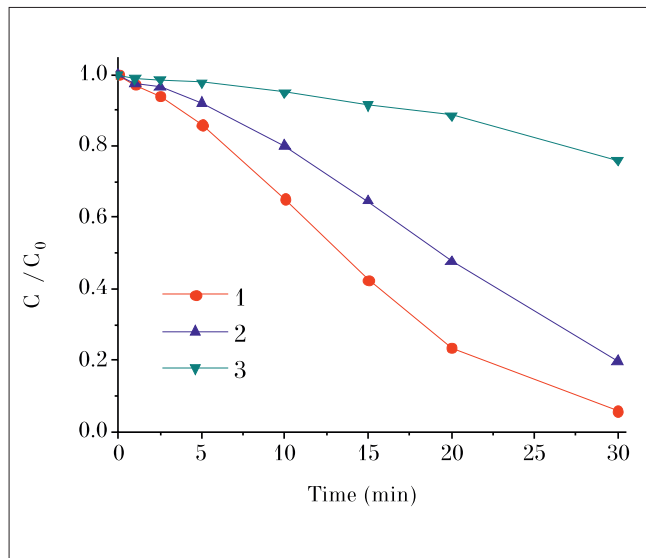


Fig. 5. The effect of AO7 concentration (mg/L): (1) 20, (2) 30, (3) 50

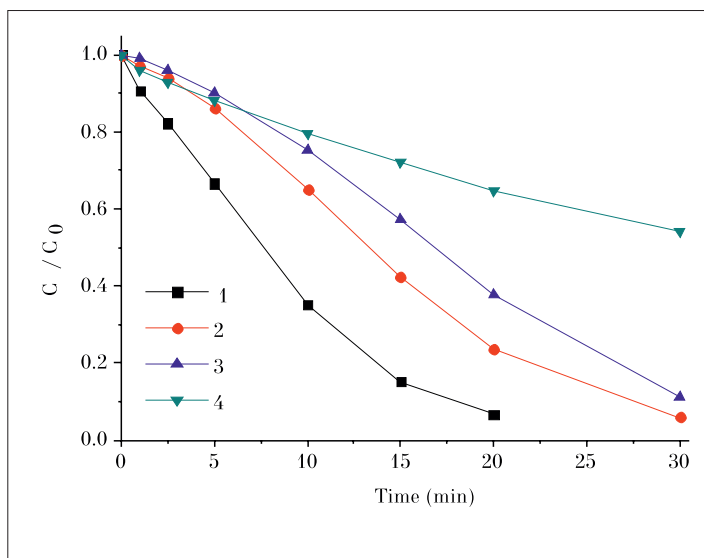


Fig. 6. The effect of pH: (1) 2.75, (2) 4.75, (3) 6.26, (4) 8.12

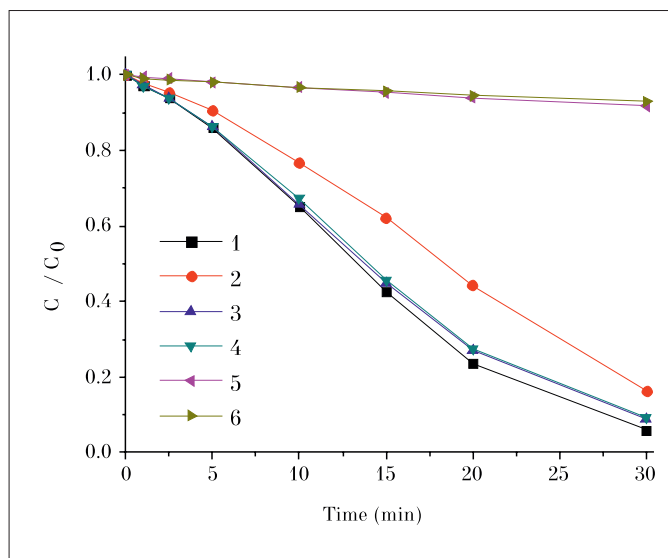


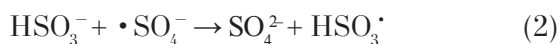
Fig. 7. The effect of negative ions on the initial rate: (1) Control, (2) NO_3^- , (3) Cl^- , (4) SO_4^{2-} , (5) HCO_3^- , (6) HPO_4^{2-}

pH 4.75 and the light intensity 500 W. When PS concentration increased from 0 to 0.2 g/L, the removal efficiency of AO7 increased from 29% to 94% within 30 min. However, further increase of the PS dosage to 0.4 g/L resulted in a slight increase to 95%.

Then, keeping the concentration of PS at 0.2 g/L, the effect of various HSO_3^- dosages on the AO7 degradation was studied in the subsequent experiments.

Effect of HSO_3^- concentration

The effect of HSO_3^- concentration on AO7 degradation efficiency was evaluated by conducting experiments at 0.5, 1, 2 and 4 mM, respectively. The initial AO7 concentration was fixed at 20 mg/L, PS concentration was 0.2 g/L, initial pH was 4.75 and the light intensity was 500 W. As shown in Figure 4 (see color insert), when HSO_3^- concentration varied from 0.5 to 2 mM, the removal efficiency of AO7 within 30 min reaction increased from 88% to 94%. The higher efficiency of AO7 removal at the higher HSO_3^- dosage might due to more radicals produced in the reaction. However, further increasing the HSO_3^- concentration to 4 mM resulted in a decrease of AO7 degradation to 87%. This can be explained by the unfavorable consumption of sulfate radicals by the excessive dosage of HSO_3^- , which could react with sulfate radicals (Eqs. (2) and (3)) [15].



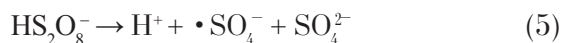
Therefore, 2 mM HSO_3^- is required to effectively activate PS to generate a sufficient amount of radicals in the process.

Effect of different initial concentrations of AO7

The initial concentration was 20, 30, and 50 mg/L, respectively, and the changes of AO7 relative concentration as a function of reaction time was shown in Figure 5 (see color insert). Even though the initial AO7 concentration is different, the degradation of AO7 has an identical trend of concentration decay as the reaction time. However, the higher the initial AO7 concentration is, the longer it takes to reach the same residual concentration (C/C_0), and the degradation efficiency decreased from 94 to 80% and to 24% within 30 min with increasing of the initial AO7 concentration, implying that the apparent rate of AO7 degradation decreases. This may be explained that the visible light transmittance could be decreased due to an increase of AO7 concentration in the solution, which led to scattering and shielding of the light.

Effect of initial pH

The solution pH can significantly affect degradation of organic pollutants in chemical oxidation processes. The effect of initial pH experiments were conducted over a wide pH range. Four levels of pH (2.75, 4.75, 6.26 and 8.12) were prevailed to evaluate the pH effect on AO7 degradation in Vis/ HSO_3^- /PS system under condition of 0.2 g/L PS, 2 mM HSO_3^- and 500 W visible light. As depicted in Figure 6 (see color insert), the best performance of Vis/ HSO_3^- /PS was observed in pH 2.75 with 93% decolorization efficiency of AO7 within 20 min, and 94%, 89% and 46% at initial pH 4.75, 6.26 and 8.12 within 30 min, respectively. In acidic condition with high concentration of protons, the generation of sulfate radical was enhanced through acid-catalyzation in accordance with Eqs. (4) and (5).



Effect of co-existing inorganic anions

Inorganic anions is usually present in real dye-containing wastewater, which may affect the efficiency of dye degradation reaction. To investigate the effects of the inorganic anions, such as HSO_3^- , SO_4^{2-} , Cl^- , HCO_3^- and HPO_4^{2-} , a series of experiments were conducted, and the results are given in Figure 7 (see color insert). It can obviously be found that SO_4^{2-} and Cl^- slightly affected the degradation of AO7 in HSO_3^- /PS/Vis system, and NO_3^- had certain influence on the AO7 degradation from 94% to 84% within 30 min. However, the addition of HCO_3^- and HPO_4^{2-} rather significantly inhibited the degradation of AO7 in Vis/ HSO_3^- /PS process.

However, the addition of HSO_3^- and HPO_4^{2-} almost completely inhibited the degradation of AO7 in Vis/ HSO_3^- /PS process. Their inhibiting effects can be ranked from low to high in an order of $\text{Cl}^- \approx \text{SO}_4^{2-} < \text{NO}_3^- < \text{HCO}_3^- \approx \text{HPO}_4^{2-}$.

As the previous reports that phosphate and bicarbonate are efficient scavengers of hydroxyl radicals [16]. HCO_3^- and HPO_4^{2-} may act as radical scavengers, resulting in the inhibition of AO7 degradation.

Conclusion

In this study, the degradation of AO7 by HSO_3^- /PS/Vis treatment process was investigated. It was demonstrated that aqueous solutions of AO7 could be degraded in the HSO_3^- /PS/Vis process, in which the efficiency was enhanced greatly under the visible light. The optimal conditions were initial AO7 concentration 20 mg/L, PS concentration

0.2 g/L, HSO_3^- concentration 2 mM and Vis light 500 W. The effects of the inorganic anions that likely influence the degradation rate in $\text{HSO}_3^-/\text{PS}/\text{Vis}$ system were also investigated. NO_3^- , HCO_3^- and HPO_4^{2-} had a negative effect on AO7 degradation efficiency in $\text{HSO}_3^-/\text{PS}/\text{Vis}$ process. All of these results show that $\text{HSO}_3^-/\text{PS}/\text{Vis}$ is a simple and efficient oxidation technology for the remediation of wastewaters containing azo dyes. The obtained results will be useful for designing the energy-resource-saving chemical processes of water management systems of industrial plants according to the methodology [17–21].

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