

## ВЛИЯНИЕ АКЦЕПТОРОВ РАДИКАЛОВ И СХЕМА ДЕСТРУКЦИИ АЗОКРАСИТЕЛЯ В ВОДНЫХ РАСТВОРАХ В ПРИСУТСТВИИ ИОНОВ ЖЕЛЕЗА (III) И ПЕРСУЛЬФАТА

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*Изучена деструкция красителя кислотного оранжевого-7 (АО7) в водных растворах при воздействии иона железа (III), активации процесса окисления ионом персульфата (PS,  $S_2O_8^{2-}$ ) и воздействии видимого излучения (Vis) ( $\geq 420$  нм). Исследован эффект поглощения радикалов с использованием этанола (EtOH), трет-бутилового спирта (ТВА) и азиды натрия с целью установления того, что гидроксильный радикал ( $\cdot OH$ ) является основным активным окислителем АО7, приводящим к его обесцвечиванию, в то время как сульфат радикал ( $SO_4^{\cdot -}$ ) и синглетный кислород ( $^1O_2$ ) также вносят свой вклад в процесс деструкции красителя. Промежуточные продукты реакции определяли с помощью метода масс-спектрометрии с ионизацией электрораспылением (ESI-MS), в результате чего был предложен вероятный механизм деструкции. Высказано предположение о том, что на начальной стадии радикал атакует атом азота красителя, при этом в результате одновременного разрыва двух связей C-N краситель деструктирует на п-фенолсульфо кислоту и 1,2-нафтахинон. Далее имеет место последующее окисление этих продуктов с потерей группы  $-SO_3^-$ . На заключительных стадиях в результате раскрытия центрального кольца образуются ациклические карбоксильные кислоты, и дальнейшее окисление, очевидно, приводит к образованию простых карбоксильных кислот. Результаты исследования могут быть полезными для создания простой, эффективной и экономичной системы деструкции трудно биоразлагаемого азокрасителя. Даны рекомендации по организации эффективного контроля качества отводимой технологической воды и продуктов ее обработки на локальных очистных сооружениях промышленного предприятия с целью предотвращения попадания вредных биологических веществ в гидросферу.*

**Ключевые слова:** деструкция красителя, краситель кислотный оранжевый 7, акцепторы радикалов, промежуточные продукты реакции, путь деструкции, минерализация

## EFFECT OF RADICAL SCAVENGERS AND PROPOSED PATHWAYS FOR DEGRADATION OF AZO DYE IN AQUEOUS SOLUTION UNDER PRESENCE OF IRON(III) AND PERSULPHATE

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*The degradation process of Acid Orange 7 (AO7) in aqueous solutions by iron(III) under activation by persulfate (PS,  $S_2O_8^{2-}$ ) oxidation and Visible (Vis) light ( $\geq 420$  nm) exposure has been studied. The radical scavenging effect was examined by using ethanol (EtOH), tert-butyl alcohol (TBA) and sodium azide to state that the hydroxyl radical ( $\cdot OH$ ) is regarded as the predominant reactive oxidant for the AO7 decolorization, while the sulfate radical ( $SO_4^{\cdot -}$ ) and singlet oxygen ( $^1O_2$ ) are also make their contribution to dye's degradation. The reaction intermediates were determined by electrospray ionization-mass spectrometry (ESI-MS) analysis, and a probable degradation pathway mechanism has been proposed. It was suggested, that firstly an initial successive radical attacks the N atom of the dye, which decompose to p-phenolsulfonic acid and 1,2-naphthaquinone through the contemporaneous break of two C-N bonds. Afterwards, subsequent oxidation of these products and loss of the  $-SO_3^-$  group are observed. Finally, the acyclic carboxylic acids are formed from the central ring-opening, and then the further oxidation to simple carboxylic acids is evident. The work can provide a simple, effective and economic system for the treatment of non-biodegradable azo dye. The recommendations were proposed on organization of an effective quality control of technological water discharge and products of its processing at the local wastewater treatment facilities of industrial plants for prevention of the ingress of hazardous biological substances to the hydrosphere.*

**Key words:** dye's degradation, Acid Orange 7, radical scavengers, reaction intermediates, degradation pathway, mineralization

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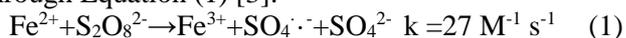
### INTRODUCTION

Earlier the degradation of Acid Orange 7 (AO7) in aqueous solutions by iron(III) under activation by persulfate (PS,  $S_2O_8^{2-}$ ) oxidation and Visible (Vis) light ( $\geq 420$  nm) exposure was performed by us.

The efficiency of different systems including iron(III) under Vis light irradiation ( $Fe^{3+}/Vis$ ),  $Fe^{3+}/PS$ ,  $PS/Vis$  and  $Fe^{3+}/PS/Vis$  has been evaluated. It was found that the efficiency of  $Fe^{3+}/PS$  and  $PS/Vis$  system was low, and only about 48% of AO7 was oxidized within 20 min of experiment time under  $Fe^{3+}/Vis$  system action,

and it was further improved to almost 95% within 20 min by Fe<sup>3+</sup>/PS/Vis system. Various process-dependent parameters, such as PS, Fe<sup>3+</sup>, dye concentration as well as initial pH were investigated to optimize the process. As results indicated, the dye's degradation efficiency increased with the increase of PS and Fe<sup>3+</sup> concentration over the tested range.

As a common oxidant, HO· radical has a redox potential of 1.8-2.7 V vs. NHE (normal hydrogen electrode) [1]. While SO<sub>4</sub><sup>·-</sup> radical demonstrates the same or even higher redox potential equal to 2.5-3.1 V vs. NHE [2], which is generated in PS/Fe<sup>2+</sup> process through Equation (1) [3].



In this work, the primary reactive oxidants and the finite degradation products of AO7 in the Fe<sup>3+</sup>/PS/Vis process were investigated to propose pathways for degradation of AO7.

## EXPERIMENTAL

### Materials

Acid Orange 7 (AO7, C<sub>16</sub>H<sub>11</sub>N<sub>2</sub>NaO<sub>4</sub>S) was purchased from Aladdin Industrial Corporation. Iron(3+) nitrate nonahydrate (Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O), sodium persulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>), tert-Butyl alcohol (TBA, AR), ethanol (EtOH, AR) 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. The spin trap reagent 5, 5-dimethyl-1-pyrroline-N-oxide (DMPO) was purchased from Sigma Chemical Co. 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 Fe<sup>3+</sup>. 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<sub>0</sub>) 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 3.46, no adjustment). Before the beginning of reaction, PS solution and Fe<sup>3+</sup> solution were added to the reactor.

### Analysis

To monitor the degradation process of AO7, solution samples were taken out at predetermined 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 photodegraded azo-dye, which was calculated from the following Equation (2):

Decolorization efficiency (%) = (C<sub>0</sub> - C<sub>t</sub>) / C<sub>0</sub> · 100, (2) where C<sub>t</sub> is the absorbance at 484 nm for AO7 at reaction time t and C<sub>0</sub> is the related initial absorbance.

The formation of short-lived radicals during AO7 decolorization was detected by ESR spin-trapping technique at room temperature using a Bruker ESR A-300 spectrometer with the following parameters: center field 3516 G, sweep width 100 G, microwave frequency 9.86 G, modulation frequency 100 kHz, microwave power 1 mW.

The intermediate products during AO7 degradation reaction were analyzed by mass spectrometry, and the experiments were performed on an Esquire LC-ion trap mass spectrometer (Bruker Daltonics, Bremen, Germany) equipped with an orthogonal geometry ESI source. Nitrogen was used as the drying (3 L/min) and nebulizing (6 psi) gas at 300 °C. The spray shield was set to 4.0 kV and the capillary cap was set to 4.5 kV. Scanning was performed from m/z 90 to 400 in the standard resolution mode at a scan rate of 13 kDa/s. Before analysis, each sample was diluted ten times.

## RESULTS AND DISCUSSION

### Radical detection

In order to understand the reaction mechanism, the formation of short-lived radicals during AO7 decolorization was detected by ESR spin-trapping technique. The measured ESR spectra before and after reaction are displayed in Fig. 1.

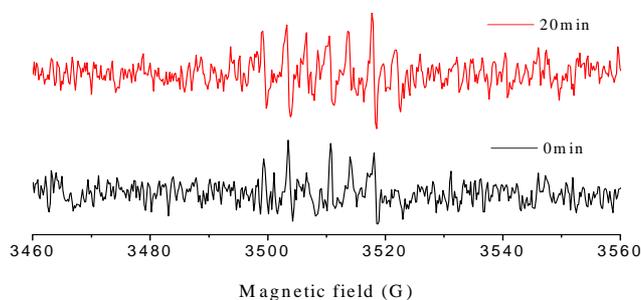


Fig. 1. DMPO spin-trapping ESR spectra at different time, min: 0 (1), 20 (2)

Рис. 1. ЭПР спектры ДМПО-спинового улавливания для интервалов времени, мин: 0 (1), 20 (2)

The ESR spectrum of DMPO-OH or DMPO-SO<sub>4</sub> was not observed but a narrow spectrum appeared to be the DMPO oxidation product, DMPO-X, which might come from the reaction of DMPO with ·OH and/or SO<sub>4</sub><sup>·-</sup> radicals.

*Effect of radical scavengers*

To evaluate the contribution of the free radicals, three kinds of radical scavengers were employed: ethanol (EtOH), tert-butyl alcohol (TBA) and sodium azide (NaN<sub>3</sub>). As indicated in Fig. 2, the addition of 1 M EtOH significantly suppressed the oxidation process with AO7 removal efficiency declining from 95% to 41% in 20 min reaction. EtOH contains α-hydrogen which can rapidly quench both SO<sub>4</sub><sup>·-</sup> and ·OH. The reaction constants of EtOH with SO<sub>4</sub><sup>·-</sup> and ·OH are 1.6-7.7·10<sup>7</sup> M<sup>-1</sup> s<sup>-1</sup> and 1.2-2.8·10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup>, respectively [4]. Consequently, the presence of EtOH led to the consumption of reactive radicals and the decrease of removal efficiency. ·OH can be generated via the reaction of SO<sub>4</sub><sup>·-</sup> and water. In order to investigate the contribution of ·OH to the AO7 removal in Vis/Fe<sup>3+</sup>/PS process, TBA was introduced. TBA can quickly quench ·OH with the reaction constant 3.8-7.6·10<sup>8</sup> M<sup>-1</sup> s<sup>-1</sup>, which is much more than the rate constant of TBA with SO<sub>4</sub><sup>·-</sup> (4.0-9.1·10<sup>5</sup> M<sup>-1</sup> s<sup>-1</sup>). Hence TBA is generally used as ·OH scavenger [4]. As observed in Fig. 2, the addition of 1 M TBA inhibited the oxidation process moderately with removal efficiency of AO7 decreased from 95% to 69% in 20 min reaction. The addition of 0.4 g/L sodium azide, which is a scavenger of both oxygen and hydroxyl radicals [5], results in almost complete inhibition of the degradation process.

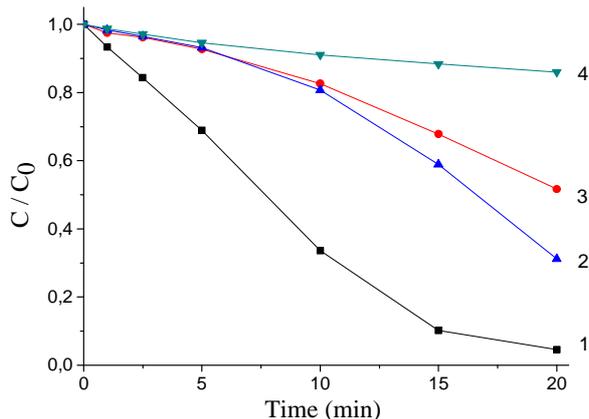


Fig. 2. The effect of radical scavengers: None (1), 1M EtOH (2), 1M TBA (3), 0.4 g/L NaN<sub>3</sub> (4)

Рис. 2. Эффективность присутствия акцепторов радикалов: отсутствие (1), 1M EtOH (2), 1M TBA (3), 0,4 g/L NaN<sub>3</sub> (4)

Compared with the control experiment, the addition of 1 M TBA resulted in 26% AO7 decay drop, while 54% AO7 decay drop was obtained by the addition of 1 M EtOH, and besides, sodium azide almost

inhibited the degradation process. These results provide evidence that ·OH is the major radical species participating in the AO7 decolorization process, and SO<sub>4</sub><sup>·-</sup> and <sup>1</sup>O<sub>2</sub> are also involved, but its contribution is minor compared with ·OH.

*Photodegradation Products and Proposed Pathways*

Direct-infusion electrospray ionization mass spectrometry (ESI-MS), which has been the technology of the choice for detection and identification of reactants, products, and intermediates in solution, [6] was applied to screen for intermediate products during AO7 degradation with Vis/Fe<sup>3+</sup>/PS system.

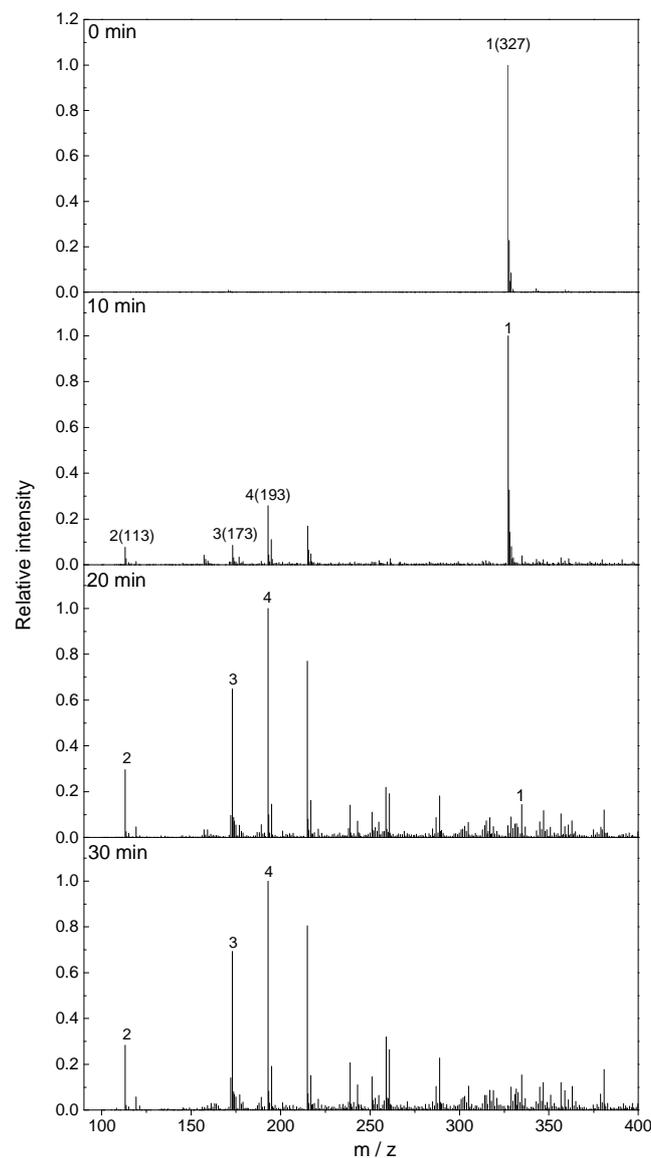


Fig. 3. ESI (-) mass spectra of AO7 solution under degradation with Vis/Fe<sup>3+</sup>/PS system at different time (min): 0 (a), 10 (b), 20 (c), 30 (d). The peak values: 327 (1), 113 (2), 173 (3), 193 (4)  
 Рис. 3. ESI - масс-спектры с отрицательной ионизацией раствора AO7 при его деструкции в системе Vis/Fe<sup>3+</sup>/PS для интервалов времени: 0 (a), 10 (b), 20 (c), 30 (d). Положения пиков: 327 (1), 113 (2), 173 (3), 193 (4)

Fig. 3 displays the representative spectra in the negative ion model from 0 to 30 min.

The molecular weight of AO7 was 350 with the structure shown in Fig. 5, and in aqueous solution the  $\text{RSO}_3\text{Na}$  groups in the dye will dissociate into  $\text{RSO}_3^-$  and  $\text{Na}^+$  ions. At the beginning of the reaction, an intense ion of  $m/z$  327 corresponding to AO7  $[\text{M}-\text{Na}]^-$  was observed as expected. After 20 min treatment, the intensity of AO7 at  $m/z$  327 decreased significantly, indicating that it was degraded into some intermediate products. The signal peaks at  $m/z$  113, 173 and 193 showed up. According to the values of  $m/z$  173 and the suggested structures, this product can be regarded as *p*-phenolsulfonic acid (*p*-PSA), which can be found as a common product that comes from the destruction of AO7 to those reported previously [7, 8]. The intermediate product could then be continually oxidized to the ions of  $m/z$  193, and  $m/z$  113 may come from the loss of  $-\text{SO}_3^-$  group. With the reaction proceeding AO7 was further degraded to the mentioned products as the relative intensity of these ions increased after 30 min.

Positive ionization mode was also tested to detect positively charged species, and the results are shown in Fig. 4. At the beginning of the reaction, an intense ion of  $m/z$  373 was corresponded to AO7  $[\text{M}+\text{Na}]^+$ , which was identical with the result of  $[\text{M}-\text{Na}]^-$  at  $m/z$  327. After 30 min of incubation, new peaks at  $m/z$  181, 165, 219, 261 and 275 were observed. The ions  $m/z$  181, 219 and 165 could be attributed to 1,2-naphthaquinone and its further oxidized compounds. Besides,  $m/z$  275 may be the product with the radical attacking and further oxidation of the ion  $m/z$  261, 165. From the +MS data at different reaction times, it was found that the amount of 1,2-naphthaquinone increased to the highest value at 10 min and then decreased. According to the literature, the toxicity of naphthaquinone from AO7 degradation is even higher than that of the azo dye [9]. Fortunately, the compound can be easily degraded by Vis/ $\text{Fe}^{3+}$ /PS system. It should be noted that the observation of ions after a long reaction time does not mean the later of their appearing as the detection of ions by ESI-MS is not only related with its concentration but also with its degree of ionization.

Consequently, a reaction sequence for photo-degradation of AO7 by Vis/ $\text{Fe}^{3+}$ /PS system was proposed on the above analyses of ESI-MS data, and is shown in Fig. 5. First, an initial successive radical attacked on the N atom of the dye, which decomposed to *p*-PSA and 1,2-naphthaquinone through the contemporaneous break of two C-N bonds. Afterwards, subse-

quent oxidation of these products and loss of the  $-\text{SO}_3^-$  group. Finally, the acyclic carboxylic acids were formed from the central ring-opening, and then were further oxidized to simple carboxylic acids. The organization of an effective quality control of technological water discharge and products of its processing at the local wastewater treatment facilities of industrial plants prevent the ingress of hazardous biological substances to the hydrosphere. This quality control is of particular significance when the reuse of treated wastewater and of wastewater processing products is provided [10].

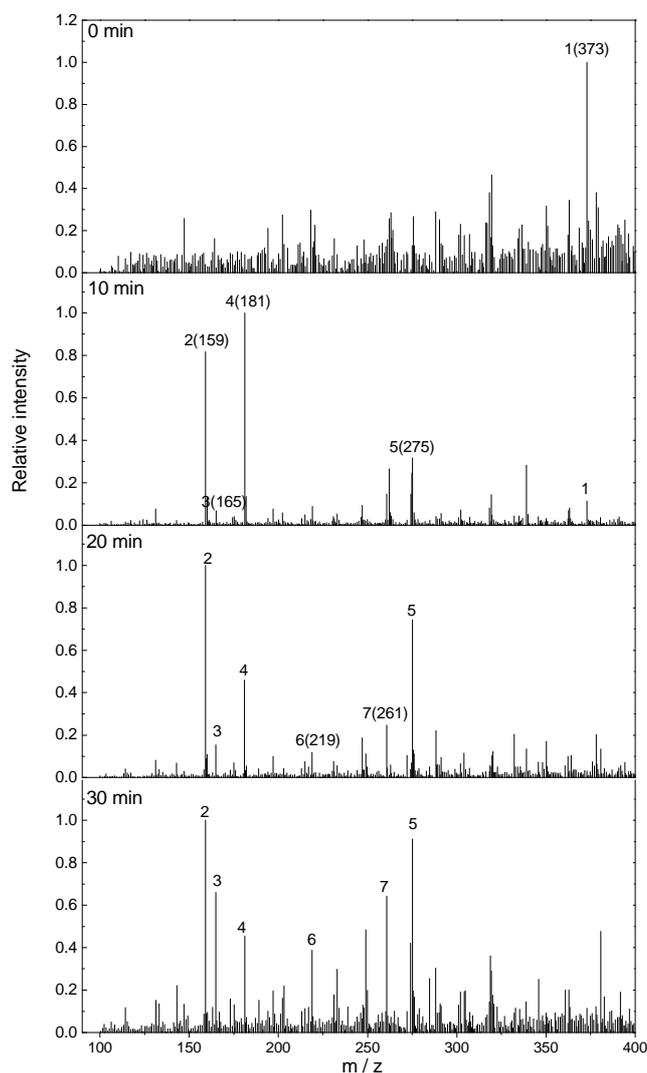


Fig. 4. ESI (+) mass spectra of AO7 solution under degradation with Vis/ $\text{Fe}^{3+}$ /PS system at different time (min): 0 (a), 10 (b), 20 (c), 30 (d). The peak values: 373 (1), 159 (2), 165 (3), 181 (4), 275 (5), 219 (6), 261 (7)

Рис. 4. ESI - масс-спектры с положительной ионизацией раствора AO7 при его деструкции в системе Vis/ $\text{Fe}^{3+}$ /PS для интервалов времени: 0 (а), 10 (б), 20 (в), 30 (д). Положения пиков: 373 (1), 159 (2), 165 (3), 181 (4), 275 (5), 219 (6), 261 (7)

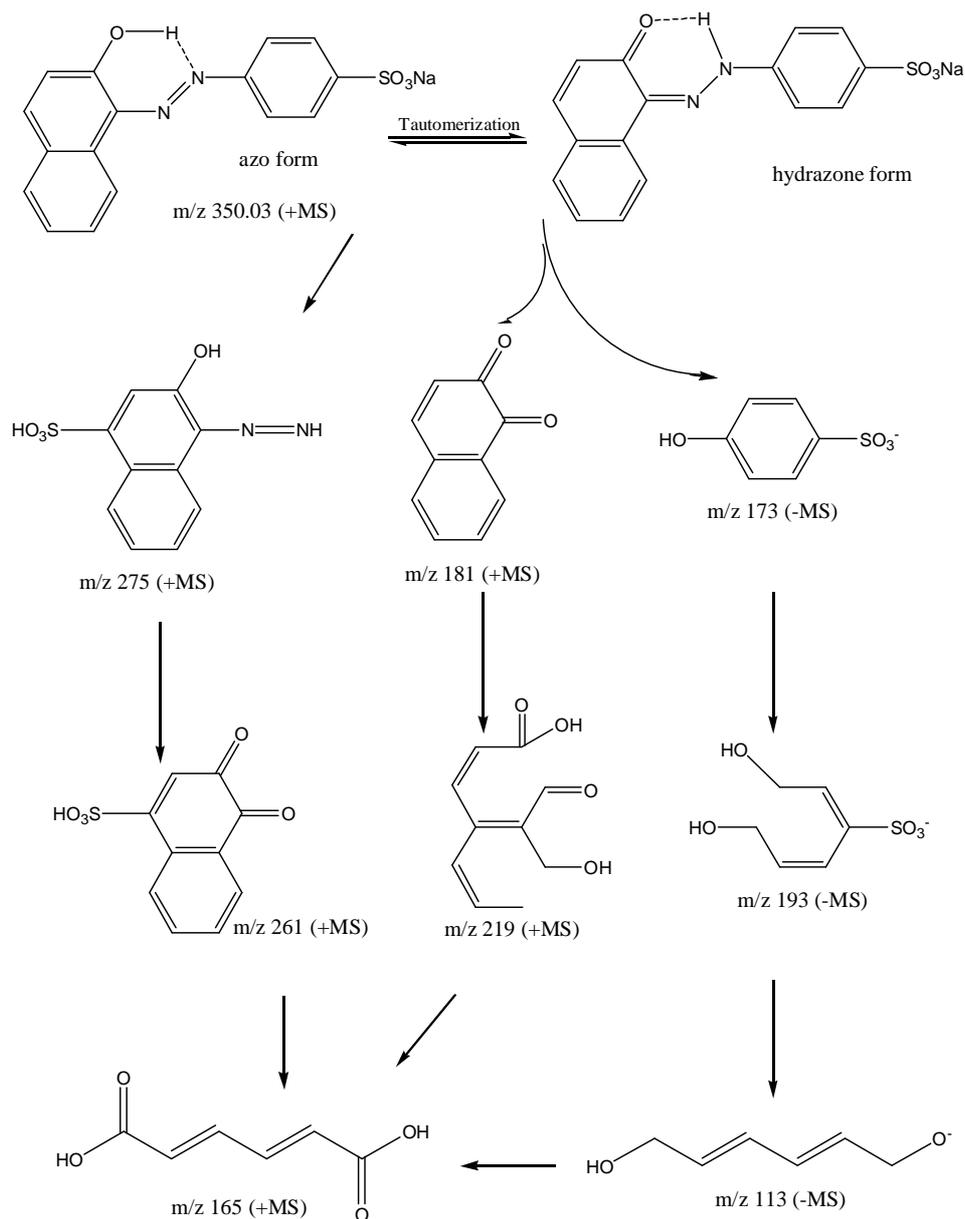


Fig. 5. The scheme of proposed pathway for the degradation of AO7 by Vis/Fe<sup>3+</sup>/PS process  
Рис. 5. Схема предложенного механизма деградации АО7 в процессе Vis/Fe<sup>3+</sup>/PS

### CONCLUSION

In this study, the mechanistic details of AO7 degradation by Fe<sup>3+</sup>/PS under Vis light was investigated, with a particular emphasis on AO7 degradation pathways. The presence of EtOH, TBA and NaN<sub>3</sub> hindered the degradation of AO7, indicating that ·OH is the major radical species participating in the AO7 decolorization process, and SO<sub>4</sub><sup>·-</sup> and <sup>1</sup>O<sub>2</sub> are also involved. Based on the ESI-MS analysis of the degradation intermediates, a pathway was proposed for the AO7 degradation. The C-N bonds of AO7 was attacked by the radicals, and smaller compounds, such as p-PSA, 1,2-naphthaquinone acid and simple carboxylic acids, were formed.

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