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Photo-degradation of methylene blue in the presence of 2-anthraquinone sulfonate and cyclohexanol

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ABSTRACT

Hydroxyl radical is a highly reactive oxygen species and can be used to oxidize many pollutants and toxic organic compounds. 2-Anthraquinone sulfonate (2-AQS) was found capable of producing hydroxyl radicals under UVA exposure. In this study, the photo-induced oxidative degradation of methylene blue (MB) by 2-anthraquinone sulfonate was investigated. Results indicated that 2-anthraquinone sulfonate was able to photo-degrade methylene blue. Addition of some chemical such as cyclohexanol could significantly increase the photo-degradation of methylene blue by 2-anthraquinone sulfonate. The degradation process was investigated by using LC–MS. Potential photochemical reaction mechanism of 2-anthraquinone sulfonate was proposed in this paper. Influence of solution pH value and different ratios of 2-AQS, cyclohexanol and MB mixture on the degradation of methylene blue were also studied.

1. Introduction

Since the discovery of its photocatalytic effect in 1967 [1], TiO_2 has received wide attentions from researchers and also found broad applications in photo-oxidation of many chemicals [2]. To enhance photocatalytic oxidation functions of TiO_2, many research activities were focused on making TiO_2 into various forms possessing very high surface areas: e.g. nanoparticles [3,4], nanotubes [5,6], films [6–11], and single crystals [12]. These materials are used in wastewater treatment, air purification, antibacterial treatment, detoxification, antifogging treatment, and self-cleaning purposes. More specifically, TiO_2 was found capable of photo-degrading dyes and other organic pollutants [7,8,13–19]. Most of these degradation reactions are based on the photocatalytic generation of reactive oxygen species (ROS), which may include hydroxyl radical ($HO^{\bullet}$), superoxide anion (O_2), hydrogen peroxide (H_2O_2), and singlet oxygen ($^1O_2$)^2, particularly in aqueous systems.

While the applications of TiO_2 have captured much attention from researchers for decades, some organic compounds were found to be able to generate ROS under UV irradiation and are potential candidates for environment remediation and advanced functional materials. If a compound can generate these radicals under light exposure, it may also have the same power as TiO_2 to decompose certain organic compounds [2,20]. 2-Anthraquinone sulfonate (2-AQS) was found to produce these radicals in aqueous solutions under light exposure [21–23] and was used to degrade cellulose [24] and decolorize 2, 6-dichloroindophenol [25]. 2-AQS treated textile materials demonstrated powerful antimicrobial effects due to the generation of these radicals [26]. 2-AQS is a photo-sensitizer, similar to benzophenone. Under UV irradiation it can abstract hydrogen from the solution or other substrates to form radicals, and then these radicals can lead to formation of reactive oxygen species or even radical polymerization of monomers whichever is possible. In a previous paper, a radical grafting reaction on polyamide surfaces initiated by surface immobilized 2-AQS was reported [27], which is an example of photo-induced radical graft polymerization. Since the thus formed 2-AQS radicals can react with oxygen to form ROS [21–23], compounds which have weaker C–H bonds than O–H of water could enhance the formation of 2-AQS radical and consequently ROS in the system. Therefore, in this study compound such as cyclohexanol was added as a co-catalyst to 2-AQS aqueous solution to assist the generation of reactive oxygen species. Here, 2-AQS was employed to photo-degrade methylene blue (MB), a common colorant, and cyclohexanol, serving as a booster, was added into the system to enhance the effect. The results showed that when cyclohexanol

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was added into a solution of 2-AQS and MB mixture, MB was degraded within hours, and solution pH value showed a vital effect on the degradation efficiency of MB. Compared with TiO_2, 2-AQS can be chemically incorporated onto surfaces of solid support materials such as polymers and fibers, which are easy to be used for wastewater treatment in practice.

2. Material and methods

2.1. Materials

2-Anthraquinone sulfonate (95%) and methylene blue (85%) were purchased from Aldrich (Milwaukee, WI). Cyclohexanol (99%) was purchased from Alfa Aesar (Ward Hill, MA). All other chemicals were used as received. Deionized water was purified by Milli-Q system (Millipore, Bedford, MA, USA) for HPLC usage. All other water used in this study was deionized water.

2.2. Apparatus and conditions

UVA irradiation was conducted in a Spectrolinker XL-1000 UV crosslinker (Spectroline, USA), with five 8 w lamps in 365 nm wavelength. The distance between UV lamps and materials is 14 cm. The UVA light intensity is 2.0 mW/cm^2.

UV–vis absorption spectra were taken with an Evolution 600 UV–visible spectrophotometer (Thermo Scientific, USA) in a wavelength range of 200–800 nm with a 1-cm quartz cell. Fourier transform infrared (FTIR) spectroscopy was performed with a Nicolet 6700 FTIR spectrometer (Thermo Scientific, USA) with a resolution of 4 cm^{-1}.

The liquid chromatography mass spectrometry (LC–MS) analyses were performed using a Waters e2695 liquid chromatography system, equipped with a Waters 2998 photodiode array (PDA) detector and Waters Micromass ZQ (ESI–MS). The flow rate was set at 0.33 mL/min and the injection volume was 5 μL. The detection wavelength was set from 190 to 800 nm. Instrument control and data acquisition were performed using a Micromass MassLynx software (version 4.1) (Waters Co., Milford, MA, USA).

The mass spectrometer conditions were as follows: capillary voltage, 3.0 kV; cone voltage, 60 eV; source temperature, 125 °C; desolvation temperature, 350 °C; desolvation gas flow, 250 L/h. A reverse phase C18 column (5 μm particle size, 4.6 by 150 mm) was used.

2.3. Procedure

6×10^{-3} M 2-AQS solution, cyclohexanol and 2×10^{-4} M methylene blue were mixed together at different volume ratios. The mixture solution was then exposed under UVA (365 nm) light for different durations. After certain time of light exposure, aliquots of mixture were taken out for LC–MS analysis. The mixture was shaken vigorously for 60 s before they were collected for LC–MS analysis. Due to the low solubility of cyclohexanol as well as its photochemical reaction products, there were both oil and water layers in the mixture. Before the analysis, all the solutions were filtered with 0.2 μm filter. The mobile phase was a mixture of 40% actonitrile (with 0.1% formic acid) and 60% water (with 0.1% formic acid). Mass data was collected under both electro-positive and electro-negative modes.

2.4. FTIR test

A droplet solution of the oil layer of the cyclohexanol and 2-AQS mixture solution before light exposure and after 3 h exposure was dropped onto a NaCl crystal and then was evenly distributed on the surface. FTIR was tested in transmission mode with a resolution of 4 cm^{-1} and 64 scans.

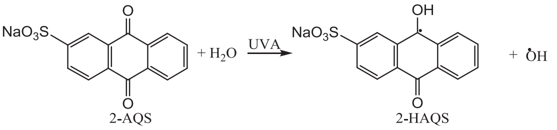
3. Results and discussion

3.1. Photochemical reaction of 2-AQS under UVA

Under UVA (365 nm) irradiation, 2-anthraquinone sulfonate (2-AQS) in aqueous solution will be excited and converted to an excited singlet molecule (2-AQS*(S)), and this singlet 2-AQS*(S) molecule then can transfer to a triplet state (2-AQS*(T)) through an intersystem crossing (Isc) process according to following equations (Eqs. (1) and (2)) [27].

$$\text{2-AQS} \xrightarrow{\text{UVA}} \text{2-AQS}^*(\text{s}) \tag{1}$$

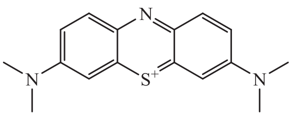
$$\text{2-AQS}^*(\text{S}) \xrightarrow{\text{Isc}} \text{2-AQS}^*(\text{T}) \tag{2}$$



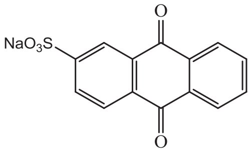
(3)

The triplet state 2-AQS molecule can abstract hydrogen from water and form a radical intermediate containing a hydroxyl group (2-HAQS, sodium 9-hydroxy-10-oxo-9, 10-dihydroanthracene-2-sulfonate), which has seven possible resonance structures (Table 1). Under UVA exposure, the color of 2-AQS aqueous solution changed from very light brownish color to bright yellow. Fig. 1 demonstrates the change of UV–vis absorbance during the UVA irradiation of the 2-AQS solution as a function of exposure time. Within the first 2 h, there was a new peak emerged between 380 and 580 nm, and the peak intensity increased with the increased exposure time. According to LC–MS results, there are four new products formed after UVA irradiation, and all of them have the same molecular weight of 303, corresponding to four isomers of an addition of one hydroxyl group to four different positions on 2-AQS. This result was same to the literature [27].

3.2. Photodegradation of methylene blue by 2-AQS



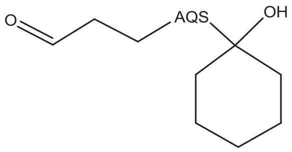
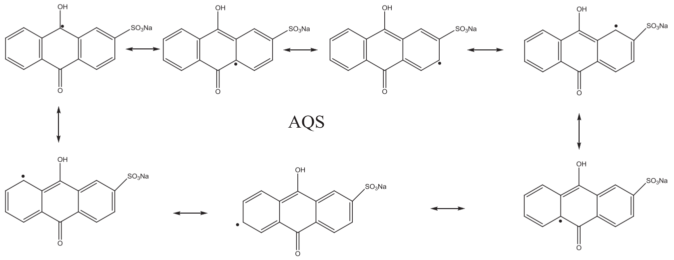
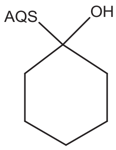
MB



2-AQS

MB is a common colorant and categorized as a basic dye (C.I. 52015). When 10 mL (2×10^{-4} M) MB solution was mixed with 1 mL of 2-AQS (6×10^{-3} M) solution, they form flocky precipitate. The so formed flocky precipitate disappeared gradually when the mixture solution was exposed to the UVA light. UV–vis spectrometer and LC–MS recorded the changes of MB and 2-AQS. Due to the existence of flocky precipitate in the mixture solution, the absorbance peak ($\lambda_{max} = 663.5$ nm) of MB changed randomly after different UVA exposure times: first the absorbance peak went up, then decreased, and finally rose again (Fig. 2) due to precipitation and resolubilization of MB in the system. The UV–vis absorbance of 2-AQS in the mixture solution was similar to that of the 2-AQS aqueous solution under different UVA exposure durations, new peaks appeared in the range 380 nm–580 nm corresponding to a yellow color.

Table 1
Photochemical reaction products based on LC–MS analysis.

Retention time	Molecular structure	Molecular weight
18.77 min		459
12.78 min		387
13.81 min		387
15.24 min		387
16.50 min		387
18.60 min		387
20.69 min		387
21.94 min		387

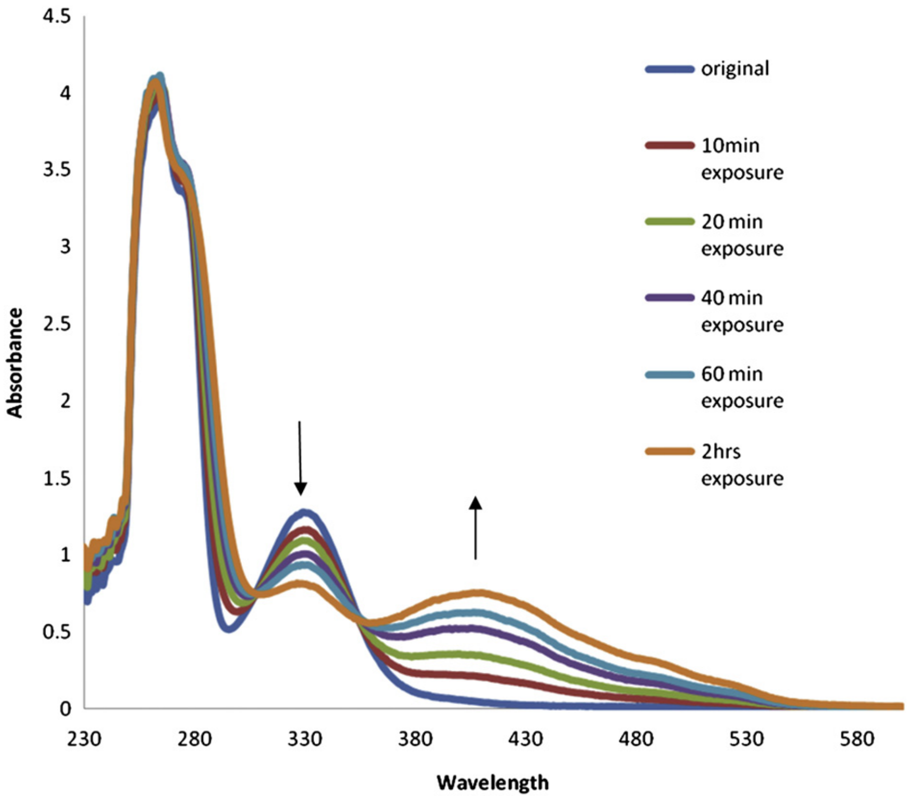


Fig. 1. UV–vis spectra of 2-AQS aqueous solution after 10 min, 20 min, 40 min, 60 min, 2 h UVA exposure, respectively.

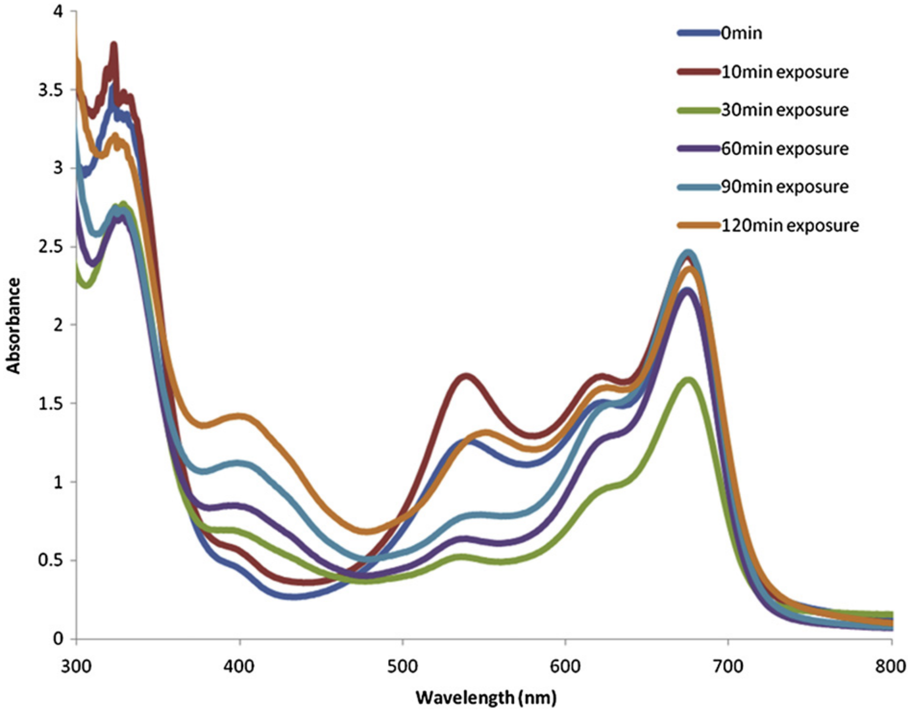


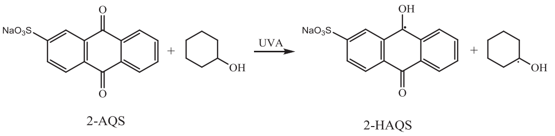
Fig. 2. UV–vis spectra of a solution of methylene blue and 2-AQS in a ratio of 10:1 after 0 min, 10 min, 30 min, 60 min, 90 min, 2 h UVA exposure, respectively.

While the UV–vis spectra showed the changes during the UVA exposures, the specific structural changes of the two chemicals were analyzed by LC–MS (Fig. 3 (I)). Retention time of MB was around 4.76 min, confirmed by the molecular weight 284 under electron positive mode and the same UV–vis spectrum of MB by the photodiode array (PDA) detector. When UVA exposure time was increased, a small new peak appeared right before the peak of MB (retention time 4.42 min), which has a molecular weight of 270, and its UV–vis spectra is very similar to MB except for the maximum absorbance showing at 648.5 nm. This is a degraded product of MB after losing one methyl group. This peak area increased gradually when the UVA exposure time was increased from 1 h to 8 h, and no trend of reduction of the peak was observed. Since this newly formed compound was quite stable under the UVA exposure, the blue color of the mixture solution stayed unchanged, indicating that 2-AQS was unable to completely photo-degrade MB.

The retention time of 2-AQS appeared at 19.74 min and five more peaks showed up in the spectra after UVA exposure (Fig. 3 (II)). The last peak appeared at around 29 min, which has a molecular weight of 319 and should be a product with two hydroxyl groups added on the original 2-AQS structure. The three peaks appeared after original 2-AQS (19.74 min) (Fig. 3 (II)) all showed new absorbance peaks from 380 to 580 nm in UV–vis range, indicating yellow or orange color for the components in the solution. Such a result also explained why a green color of the 2-AQS and MB mixture solution was formed after the light exposure, which was a result of color mixing of yellow and blue (MB) (Fig. 4). Fig. 3 (II) also showed that after 8 h UVA exposure, 2-AQS peak area was significantly decreased, and more 2-AQS related products formed in the samples with increased exposure time.

3.3. *Catalytic effect of cyclohexanol*

The above results indicated that 2-AQS was unable to completely degrade methylene blue under the UVA exposure. At this moment, a small amount of cyclohexanol as a hydrogen donor was added into the solution, and the new mixture solution was exposed to the UVA light again. The mixture was made of 1 mL 2-AQS solution (6×10^{-3} M), 1 mL cyclohexanol and 10 mL 2×10^{-4} M MB solution. The UVA (365 nm) exposure durations were 0 h, 1 h, 3 h, 5 h, and 8 h, respectively. Surprisingly, the peak of methylene blue disappeared completely after 5 h of UVA exposure (Fig. 4). HPLC results of these samples are shown in Fig. 4 (I) from bottom to top in the order of exposure time. MB has a retention time at 4.35 min, and after 60 min of UVA exposure, a small peak showed up at 4.14 min (Fig. 4). The UV–vis spectrum at 4.14 min is similar to the spectrum of MB except the maximum absorbance is at 648.5 nm instead of 663 nm. The mass spectrometer data demonstrated the weight of partially degraded MB after losing one methyl group (270). After 3 h UVA exposure, the original MB peak intensity was greatly decreased, the peak at 4.14 min increased accordingly, and another new peak appeared at 4.64 min. This peak was assigned as a product (possibly a configurational isomer) of cyclohexanol, since the same peak was observed for UVA exposed cyclohexanol and 2-AQS solution (1:5 mixture ratios). When the UVA exposure time increased to 5 h, the original MB peak completely disappeared, and only a very small peak left at 4.16 min, which demonstrated that partially degraded MB is more stable than MB. After 8 h exposure, both MB and partially degraded MB were completely eliminated. No detectable residue was found by the LC–MS.



(4)

These results revealed that cyclohexanol could significantly enhance photo-degradation power of 2-AQS in aqueous solution.

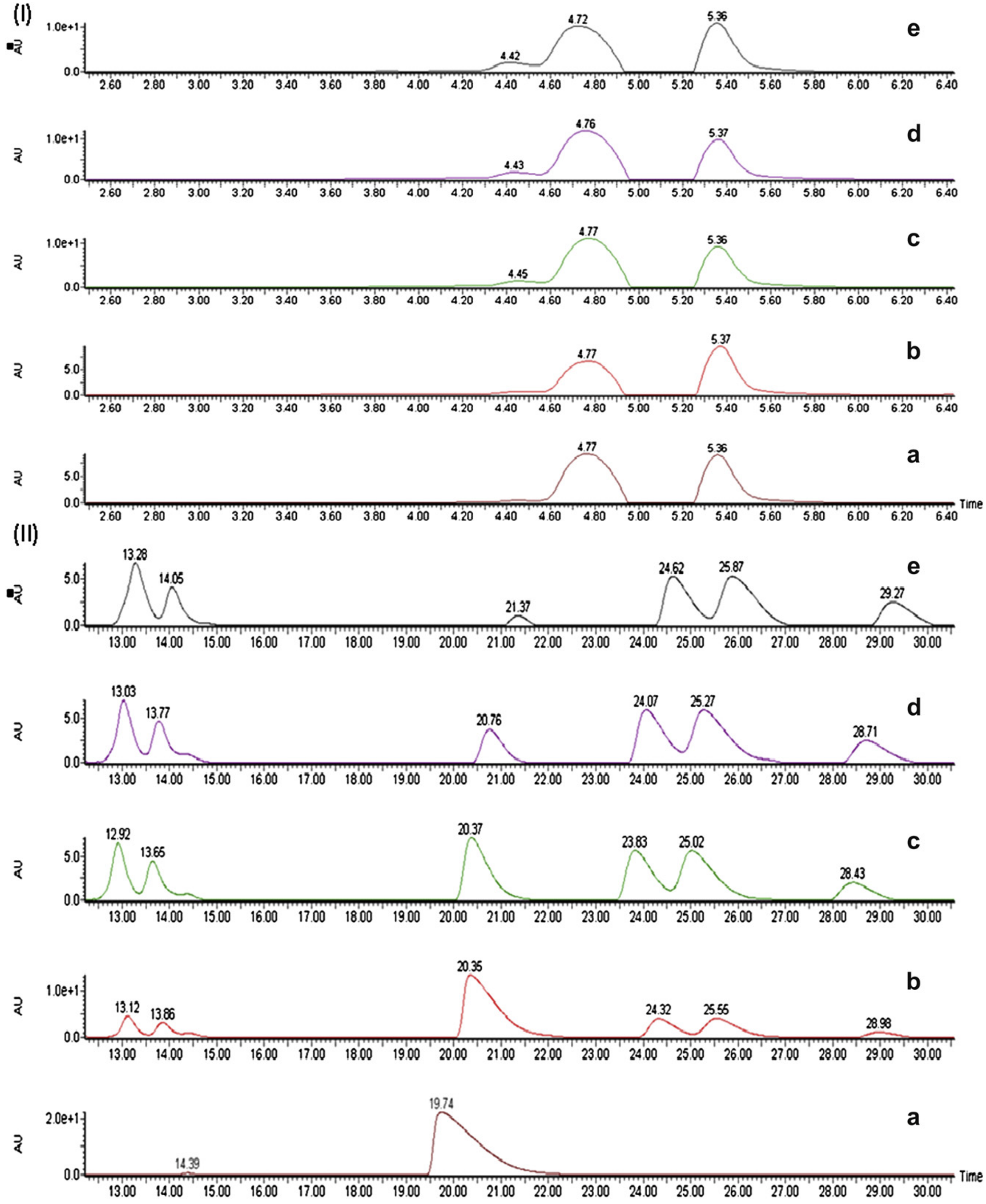


Fig. 3. HPLC results of a mixture solution of 2-AQS, cyclohexanol and MB in a ratio of 30:0:1. Peaks (I) within retention time of 2.5–6 min and (II) within 12.5–30 min: before light exposure (a), after 1 h UVA exposure (b), after 3 h exposure (c), after 5 h exposure (d), after 8 h exposure (e).

Since the bond energy of the tertiary C–H in cyclohexanol is much weaker than secondary C–H and O–H in hydroxyl group, 2-AQS could easily abstract hydrogen from the tertiary C–H to form 2-HAQS (Eq. (4)). Thus, with the existence of cyclohexanol, 2-AQS can easily form its radical intermediate, 2-HAQS. In addition, both 2-HAQS and cyclohexanol radical can combine to form a new compound in the system. LC–MS detected newly formed seven products all containing cyclohexanol (Table 1), products of coupling between 2-HAQS and cyclohexanol radical. The proposed structures of the seven products are based on the seven possible

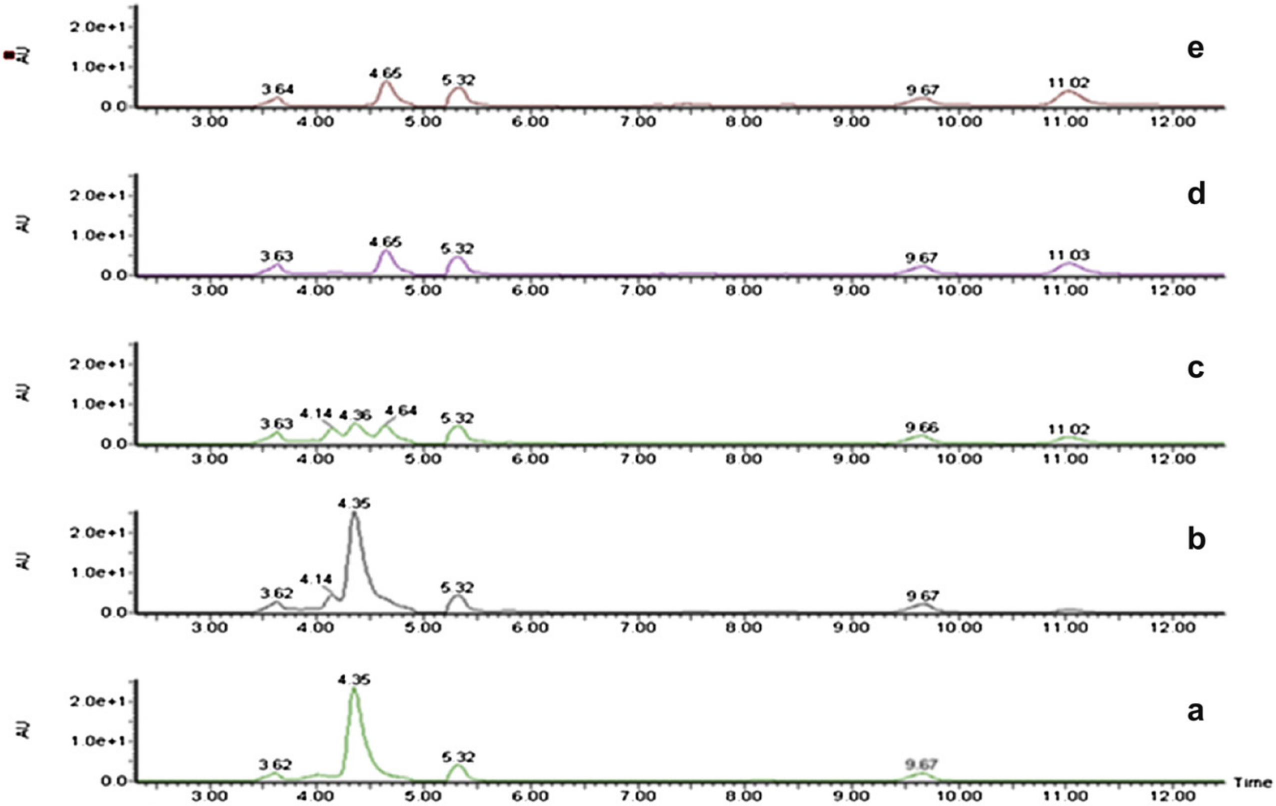
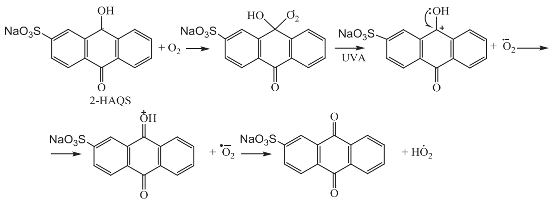


Fig. 4. HPLC results of a mixture solution of 2-AQS, cyclohexanol and MB in a ratio of 3:5:1 before UV exposure (a), after 1 h UVA exposure (b), after 3 h exposure (c), after 5 h exposure (d), after 8 h exposure (e).

resonance structures of 2-HAQS. This result further proved the proposed mechanism of formation of both 2-HAQS and cyclohexanol radicals.

If all 2-HAQS radicals combine with cyclohexanol radical, only these seven products can be found in the system. However, the reaction was carried out with existence of oxygen. 2-HAQS radical can react with O_2 to form a series of reactive oxygen species (ROS) including superoxide radicals and hydroxyl radicals [21,23]. The specific reaction pathways are shown in Eqs. (5)–(8). The hydroxyl radicals are very reactive and could easily react with MB. More ROS formed in the system due to the catalytic effect of cyclohexanol could further degrade MB and many other chemicals. According to Eq. (5), 2-AQS could be recovered after producing these ROS, a similar process to the production of hydrogen peroxide [28]. It is our hope that all 2-AQS can be recovered through the photo-active process. However, it is one of several possible photo-induced reactions.

 (5)

$$2HO_2^{\cdot} \rightarrow O_2 + H_2O_2 \quad (6)$$

$$H_2O_2 \xrightarrow{hv} 2HO\cdot \quad (7)$$

$$H_2O_2 + \dot{\bar{O}}_2 \rightarrow HO\cdot + HO^- + O_2 \quad (8)$$

3.4. *Identification of reaction products*

Based on the above mechanism, several ROS species can be produced when 2-AQS solution is exposed to light, which are responsible for degradation of MB. However, so far, except for the one that lost one methyl group, we have not seen any other fragments or products decomposed from MB from the LC–MS. It has been reported that in the presence of photocatalyst TiO_2, MB could be totally oxidized to CO_2, water and inorganic acid (Eq. (9)) that are not detectable by using regular LC–MS [29]. However, since the addition of cyclohexanol, we could use it as a probe in analysis of the reactions. Cyclohexanol radical could undergo further oxidation to form cyclohexanone. In Fig. 4, the changes of cyclohexanol peak were very clear. The major peak of cyclohexanol appeared at 9.67 min. Retention time of 4.65 min was assigned as an isomer of cyclohexanol (possibly the boat configuration). After UVA exposure, another new peak appeared at 11.03 min. Its peak intensity increased with the increasing exposure time. Meanwhile the peak intensity at 9.67 min gradually decreased. The peak at 11.03 min did not show any mass data from the ESI mass spectrometer. Its UV–vis spectrum data gave a new peak at 280 nm so the 11.03 min peak could possibly be assigned as cyclohexanone. FTIR results (Fig. 5) further confirmed this assumption. Compared with the FTIR spectrum of the original cyclohexanol and 2-AQS (1:5 mixture ratios) solution, a new peak appeared at 1704 cm^{-1}, a characteristic peak of ketone on cyclohexone.

$$MB + 25/2O_2 \rightarrow HCl + H_2SO_4 + 3HNO_3 + 16CO_2 + 6H_2O \quad (9)$$

When 2-AQS mixed with cyclohexanol and MB (2-AQS: cyclohexanol: MB = 3:5:1), the peak of 2-AQS showed at around

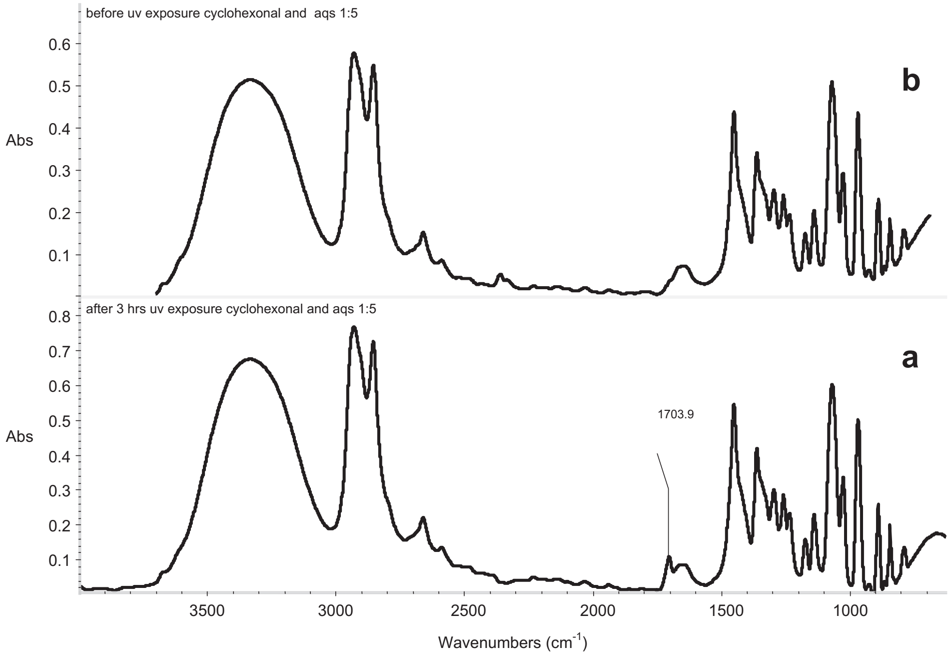


Fig. 5. FTIR of a solution of 2-AQS and cyclohexanol mixture in a ratio of 3:1 before UVA exposure (b) after 3 h exposure (a).

27.23 min. With increased UVA exposure time, the intensity decreased gradually. In addition, several small peaks appeared at 7.45 min, as well as between 13 min and 25 min after 8 h exposure. Because of the low quantity, no signal was detected from mass spectrometer for these peaks. However, when the mole ratio of three species was changed from 3:5:1 to 30:50:1, much stronger peaks appeared in this area (Fig. 6). Interestingly enough, when 2-AQS and cyclohexanol were mixed together in 3:1 ratio without methylene blue (MB), after exposed under UVA light for 3 h, the same peaks between 6 min and 32 min showed up (Fig. 6), except all peaks in the 3:1 mixture solution shifted to the left, indicating that these peaks were formed between 2-AQS and cyclohexanol, not with MB. The proposed structures for these products are listed in Table 1, all from coupling between resonance structures of 2-AQS radical and cyclohexanol radical. No monohydroxylated or dihydroxylated 2-AQS derivatives were observed in the final products, meaning that 2-AQS preferentially abstract hydrogen from cyclohexanol in this system. Thus, the above results support the proposed mechanism, i.e. cyclohexanol serves as a hydrogen donor to the photo-excited 2-AQS and promotes formation of 2-HAQS

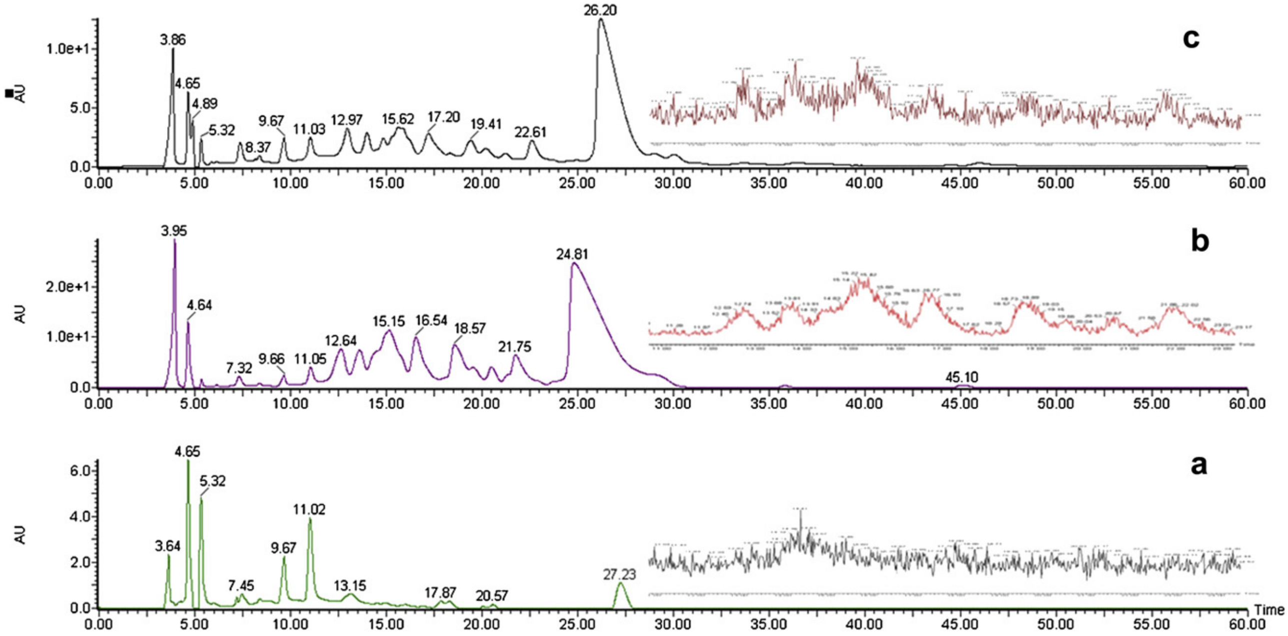


Fig. 6. HPLC results of a mixture solution of 2-AQS, cyclohexanol and MB with a mole ratio of 3:5:1 after 8 h UVA exposure (a), after 3 h UVA exposure of a solution in a mole of 3:1:0 ratio (b), after 6 h UVA exposure of a solution in a mole ratio of 30:50:1 ratio (c) (all including embedded ESI Mass data).

radical, which then react with oxygen to produce reactive ROS in the system. The ROS could degrade MB completely in the solution. The effect of cyclohexanol could be considered as a co-catalyst in the system.

3.5. Influence of pH value on degradation of methylene blue

When 2-AQS, cyclohexanol, and methylene blue were mixed in a mole ratio of 3:5:1, the solution pH value was 4.5. By adding sulfuric acid or sodium hydroxide standard solution into three mixture solutions, the pH values were adjusted to 3, 7 and 10 respectively. Degradation of methylene blue under three pH conditions was analyzed by LC–MS, and the results are shown in Fig. 7. It was found that under both acidic and neutral conditions, after 1 h of UVA exposure, the degradation of methylene blue was undetectable. However, under strong basic condition, degradation of methylene blue was more significant, with more than two thirds of methylene blue degraded in 1 h. It has been reported that under light irradiation [30,31], 2-AQS undergoes the following reactions (Eqs. (10) and (11)) in alkaline solutions, and more reactive hydroxyl radical could be generated during the process, which explains the quick degradation of methylene blue under this condition.

$$2\text{-AQS}^{*} + 2\text{-AQS} \rightarrow 2\text{-AQS}^{\cdot+} + 2\text{-AQS}^{\cdot-} \qquad (10)$$

$$2\text{-AQS}^{\cdot+} + -\text{OH} \rightarrow 2 - AQS + {}^{\cdot}\text{OH} \qquad (11)$$

3.6. Influence of amount of cyclohexanol and 2-AQS on degradation of MB

Since the co-existence of both 2-AQS and cyclohexanol in the system is necessary to provide complete degradation of MB, the impact of the ratio of 2-AQS and cyclohexanol in the mixture on the degradation reaction should be investigated. Without 2-AQS in the solution (for example, molar ratio of 2-AQS: cyclohexanol: MB = 0:50:1), after exposure to UVA, no detectable degradation of MB was found. We have discussed earlier that without cyclohexanol 2-AQS was unable to degrade MB. With addition of cyclohexanol, 2-AQS could totally degrade MB when exposed to UVA for certain time. The degradation rate was dependent on a mixture ratio. From Fig. 8 we can find that at a mixture ratio of 30:50:1, MB (showing a peak at 4.59 min) was completely degraded within 4 h of UVA exposure. When the molar ratio of 2-AQS: cyclohexanol: MB mixture was changed to 3:25:1 (Fig. 9), two more

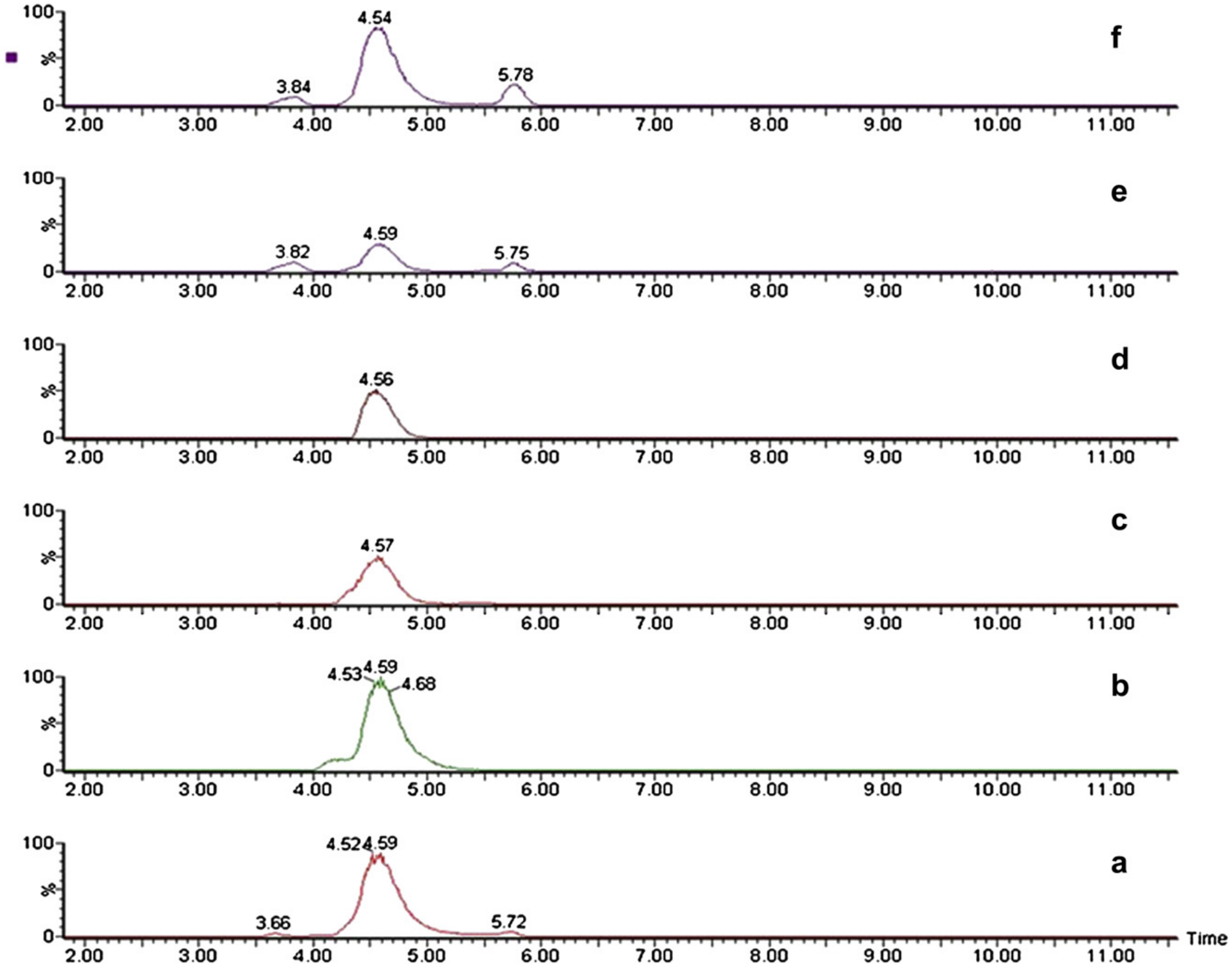


Fig. 7. Mass results of a mixture solution of 2-AQS, cyclohexanol and MB in a mole ratio of 3:5:1 at pH = 3 after 1 h UVA exposure (a), at pH = 3 before UVA exposure (b), at pH = 7 after 1 h UVA exposure (c), at pH = 7 before UVA exposure (d), at pH = 12 after 1 h UVA exposure (e), at pH = 12 before UVA exposure (f).

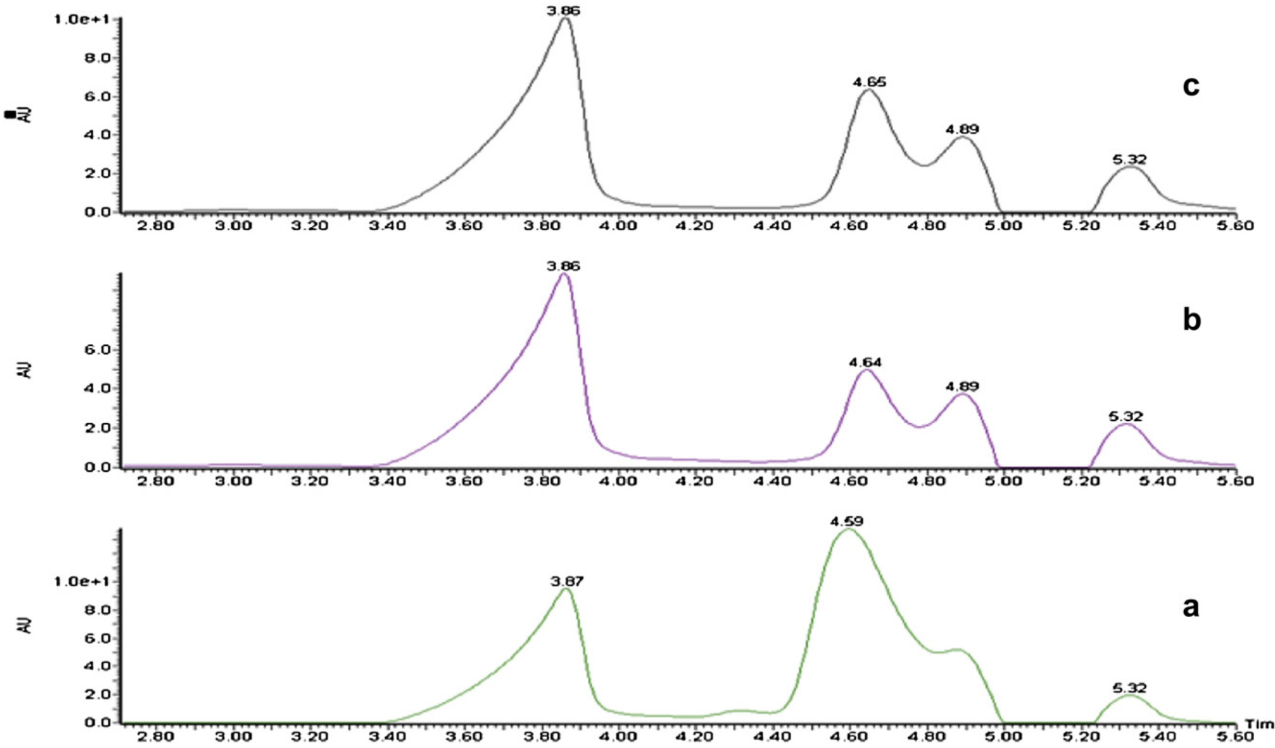


Fig. 8. HPLC results of a mixture solution of 2-AQS, cyclohexanol and MB in a mole ratio of 30:50:1 before UVA exposure (a), after 4 h UVA exposure (b), after 6 h exposure (c).

intermediates formed after 3 h UVA exposure. And after 5 h all these peaks were totally eliminated. Complete degradation of MB and its intermediates in a solution with a mixture ratio of 3:5:10 were observed after 14 h of light exposure. The results showed that increasing the ratio of either 2-AQS or cyclohexanol can result in shorter degradation time, and when methylene blue was the dominant compound in the mixture, it needs longer time to be degraded.

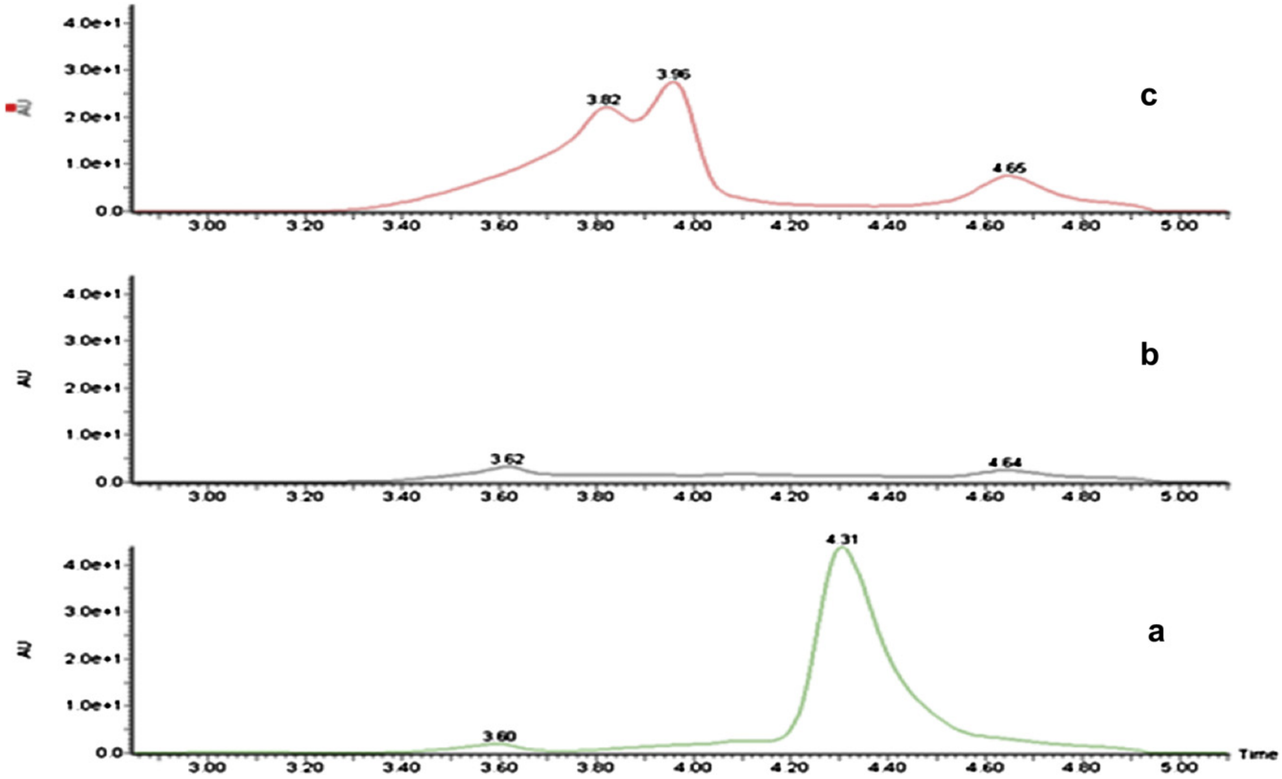


Fig. 9. HPLC results of a mixture solution of 2-AQS, cyclohexanol and MB in a mole ratio of 3:25:1 before UVA exposure (a), after 3 h UVA exposure (b), after 5 h exposure (c).

4. Conclusion

2-anthraquinone sulfonate was used to degrade MB under UVA exposure, and when some additives such as cyclohexanol was added into the aqueous solution of 2-AQS and MB, MB can be totally degraded within hours. In the process of photoreaction, some of cyclohexanol was transferred to cyclohexanone, some of it possibly became another configuration, and part of it combined with 2-AQS to form new products. Meanwhile, some 2-AQS was consumed during the photo-reactions, which is a drawback of this process. The degradation of MB is mainly caused by reactive oxygen species generated by 2-AQS under UVA. Alkaline condition favors formation of hydroxyl radicals in the system, which is the most powerful reagent that degrades methylene blue.

Acknowledgments

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