Dyes and Pigments 91 (2011) 215–224

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

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

Ning Liu, Gang Sun*

Division of Textiles and Clothing, University of California, Davis, CA 95616, USA

A R T I C L E I N F O

Article history:
Received 8 September 2010
Received in revised form
11 March 2011
Accepted 14 March 2011
Available online 21 March 2011

Keywords:
Degradation
Methylene blue
Hydroxyl radical
2-Anthraquinone sulfonate
Reactive oxygen species
Cyclohexanol

A B S T R A C T

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 ($HO^{\cdot}$), 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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* Corresponding author. Tel.: +1 530 752 0840; fax: +1 530 752 7584.
E-mail address: gysun@ucdavis.edu (G. Sun).

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doi:10.1016/j.dyepig.2011.03.018

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.

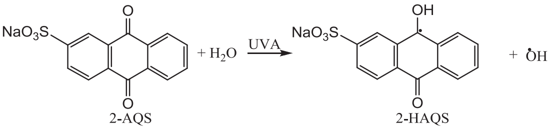
3. Results and discussion

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].

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

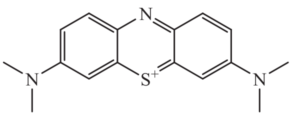
$$\text{2-AQS}^*(\text{S}) \xrightarrow{\text{Isc}} \text{2-AQS}^*(\text{T}) \quad (2)$$



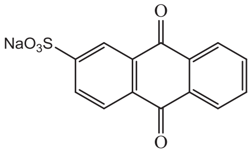
(3)

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 (λ_{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.