



Applicability of light sources and the inner filter effect in UV/acetylacetone and UV/H₂O₂ processes



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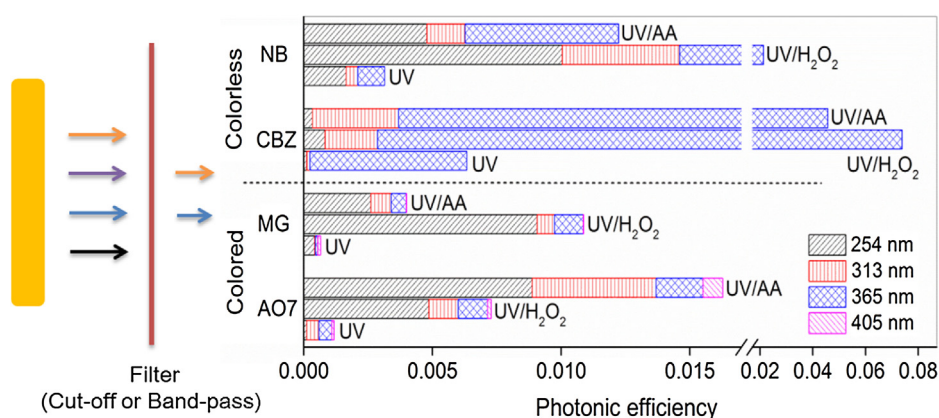
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HIGHLIGHTS

- Acetylacetone (AA) could directly use solar irradiation to decolorize dyes.
- AA had a wider applicability than H₂O₂ to a variety of light sources.
- The photonic efficiency in the UV/AA process was target-dependent.
- An accurate calculation approach for the inner filter effect was developed.

GRAPHICAL ABSTRACT



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ABSTRACT

Light source is a crucial factor in the application of a photochemical process, which determines the energy efficiency. The performances of acetylacetone (AA) in conversion of aqueous contaminants under irradiation with a low-pressure mercury lamp, a medium-pressure mercury lamp, a xenon lamp, and natural sunlight were investigated and compared with those of H₂O₂ as reference. In all cases, AA was superior to H₂O₂ in the degradation of Acid Orange 7. Using combinations of the different light sources with various cut-off and band-pass filters, the spectra responses of the absorbed photons in the UV/AA and UV/H₂O₂ processes were determined for two colored and two colorless compounds. The photonic efficiency (φ) of the two photochemical processes was found to be target-dependent. A calculation approach for the inner filter effect was developed by taking the obtained φ into account, which provides a more accurate indication of the reaction mechanisms.

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1. Introduction

Photochemical-based advanced oxidation processes (PAOPs) have attracted extensive interest with respect to the potential utilization of inexpensive and inexhaustible solar radiation [1–3]. A massive array of experimental data on the photochemical behaviors of a variety of compounds in homogeneous and heterogeneous

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systems have been reported in the literatures [4,5]. However, most of the studies involved were performed with artificial light sources, with little research conducted with solar irradiation [6,7]. The direct utilization of natural sunlight remains one of the most important scientific and technological challenges in PAOPs, because low-wavelength ultraviolet (UV) light, which is typically required to drive the related redox processes, accounts for only a small fraction (less than 5%) of the solar energy. Additionally, the weather and time fluctuations of solar radiation make it difficult to quantitatively describe the short-term kinetics of solar-driven photochemical processes. Therefore, artificial light sources are purposely employed in most PAOPs studies. For example, low-pressure (LP) and medium-pressure (MP) mercury (Hg) lamps have been widely used in the study of UV-induced PAOPs, whereas xenon (Xe) lamps are extensively used in visible light photocatalysis. Whereas LP lamps emit monochromatic light at 253.7 nm, MP-Hg and Xe light sources are not monochromatic.

In photochemical processes, the reaction kinetics and activities depend on the spectral irradiance of the light source [8–10]. Thus, in many PAOPs, a match between the absorption spectrum of the photo-activator and the emission spectrum of the light source is important for the efficient utilization of photons [11]. Efficiency spectra show the photo-response of absorbed photons by the photo-activators at the emission wavelength of the lamp [10]. To generate an efficiency spectrum, the photons absorbed should be calculated precisely. However, the application of polychromatic light sources makes it difficult to calculate the light efficiency of the photochemical processes or to gain a clear understanding of the photochemical mechanisms. Furthermore, the light-absorbing compounds compete with the photo-activators for photons, leading to the “inner filter effect” in the photochemical systems. The inner filter effect further increases the difficulty in determining the efficiency spectrum of a system irradiated with a polychromatic light source. In the literature, the inner filter effect is typically calculated based on the incident photons and absorption spectrum rather than on the photonic efficiency [12–15], mainly because the latter is usually unavailable. However, such a calculation based on the incident photons and absorption spectrum may either underestimate or overestimate the inner filter effect.

In our previous work, acetylacetone (AA) was found to be able to rapidly decolorize dyes through a non-free radical pathway with a MP-Hg lamp as the light source [16–18]. Under otherwise identical conditions, the UV/AA process exhibited an unexpectedly higher efficiency in decolorization than the UV/H₂O₂ process, but was less efficient for two colorless compounds: phenol and chlorobenzene. Based on these results, our hypothesis regarding the mechanisms in the UV/AA process was that both dyes and AA absorbed photons to form exciplexes, and that direct electron/energy transfer among the different moieties of the exciplexes led to the decolorization of the dyes [18]. Therefore, the light-absorbing property of dyes, which usually causes an unfavorable inner filter effect in the UV/H₂O₂ process, was postulated to play a positive role in the UV/AA process. The inner filter effect is expected to be related to the efficiency spectrum. However, the efficiency spectrum of the UV/AA process has remained unknown to date.

In the present work, we aimed at two objectives. The first was to determine whether the UV/AA process continues to be more efficient than the UV/H₂O₂ process when other light sources are used and to determine the photonic efficiency of AA. The second one was to develop an approach for the calculation of the inner filter effect in photochemical systems based on the obtained photonic efficiency. This calculation would allow us to determine whether the calculation of the inner filter effect without photonic efficiency would underestimate or overestimate the actual effect and to provide an unbiased assessment of the reaction mechanism.

2. Experimental section

2.1. Materials

All of the chemicals used in this study were obtained commercially and used as received. Acid Orange 7 (AO7), malachite green (MG), carbamazepine (CBZ), nitrobenzene (NB), AA, and H₂O₂ were of analytical purity grade and purchased from Sigma-Aldrich, USA. Methyl alcohol was of high performance liquid chromatography (HPLC) grade and was purchased from Merck, Germany. Short-length hydroxylated single-walled carbon nanotubes (SWCNT-OH, purity: >90%, outer diameter: 1–2 nm, length: 5–30 μm, specific surface area: 486 m²/g, hydroxyl content: 3.96 wt%) from the Shenzhen Nanotechnology Co., Ltd. (China) were used as received without further purification. Ultrapure water (18.25 MΩ cm⁻¹) prepared with a purifier (Sichuan Ulupure Industrial Co., Ltd., Sichuan, China) was used for the preparation of solutions.

SWCNT-OH stock suspensions were prepared by adding 1 mg SWCNT-OH to 100 mL ultrapure water under sonication with an ultrasonic cell crusher (JY88-II) for 4 h (the power was under 50 W). Prior to irradiation in the Homo reactor, the solutions with the SWCNT-OH were maintained in the dark for 12 h to let the adsorption to be equilibrated. The adsorption-equilibrated solutions were divided into two portions. One portion was used directly in irradiation experiments and another one was filtered through a 0.22 μm filter (Shimadzu Co., Japan) to serve as an inner filter-free control.

2.2. Irradiation experiments

Two photoreactors were used in the laboratory irradiation experiments. One was a rotating disk photoreactor (Nanjing StoneTech Electric Equipment Co., China) with a 350 W Xe lamp (Shanghai Hongguang Tungsten & Molybdenum Technology Co., Ltd., China) as the light source and a light path of 0.883 cm. A schematic of this setup is shown in Fig. S1, and the setup is referred to as the Homo reactor. Additional details on this photoreactor are available in a previous report [16]. The second photoreactor was a bench scale “collimated beam” instrument (Beijing CeAuLight Technology Co., China) with a 10 W LP-Mg lamp or a 300 W MP-Hg lamp as the light source. The MP-Hg lamp is polychromatic with primary emissions at 254, 303, 313, 365, 405, 436, 546, and 578 nm (the maximum intensity was at 365 nm and the relative intensity was shown in Fig. S2) whereas the LP-Hg lamp was monochromatic at 254 nm. The lamp was housed in a shuttered box. The sample solution was placed in an open dish underneath the shutter and was mixed with a magnetic stirrer. A schematic of this setup, referred to as the Mech reactor, is shown in Fig. S3.

The Mech reactor was employed for the determination of photonic efficiency. The light path of the Mech reactor was 4.96 cm. The cross section of the illuminated area in the Mech system was 21.2 cm². Cut-off (CF) and band-pass (BF) filters were used in the irradiation experiments. Photons of four individual wavelengths (254, 313, 365, 405 nm) and two emission bands (<365 nm and >420 nm) were obtained with a combination of lamps and filters. For the determination of photonic efficiency, the irradiation experiments were conducted under continuous N₂ bubbling.

The solar irradiation experiments were carried out on a building roof (Fig. S4) at the Xianlin Campus of Nanjing University (118°46' E, 32°03' N) on October 17, 2015.

2.3. Analytical methods

The light intensity reaching the solutions was measured with a radiometer (Photoelectric Instrument Factory of Beijing Normal University, China) that was equipped with two sensors with peak

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