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Feasibility of the UV/AA process as a pretreatment approach for bioremediation of dye-laden wastewater

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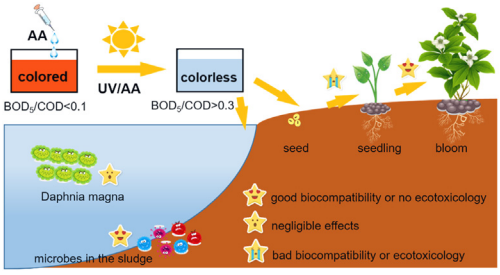
HIGHLIGHTS

- Acetylactone (AA) significantly enhanced the photo-degradation of dyes.
- The biocompatibility and toxicology of UV/AA treated solutions were investigated.
- The UV/AA process significantly improved the biodegradability of dye solutions.
- The phytotoxicity of the UV/AA process was comparable to that of the UV/H_2O_2 process.

GRAPHICAL ABSTRACT



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ABSTRACT

Biodegradability and toxicity are two important indexes in considering the feasibility of a chemical process for environmental remediation. The acetylacetone (AA) mediated photochemical process has been proven as an efficient approach for dye decolorization. Both AA and its photochemical degradation products had a high bioavailability. However, the biocompatibility and ecotoxicology of the UV/AA treated solutions are unclear yet. In the present work, we evaluated the biocompatibility and toxicity of the UV/AA treated solutions at both biochemical and organismal levels. The biodegradability of the treated solution was evaluated with the ratio of 5-d biological oxygen demand (BOD_5) to chemical oxygen demand (COD) and a 28-d activated sludge assay (Zahn-Wellens tests). The UV/AA process significantly improved the biodegradability of the tested dye solutions. Toxicity was assessed with responses of microorganisms (microbes in activated sludge and *Daphnia magna*) and plants (bok choy, rice seed, and *Arabidopsis thaliana*) to the treated solutions, which showed that the toxicity of the UV/AA treated solutions was lower or comparable to that of the UV/H_2O_2 counterparts. The results are helpful for us to determine whether the UV/AA process is applicable to certain wastewaters and how the UV/AA process could be effectively combined into a sequential chemical-biological water treatment.

1. Introduction

Dyes are widely used in several industries, such as textile and ink industries. The discharge of dye-laden wastewater into aquatic system poses threats to flora and fauna through either the inhibition of sunlight penetration or the direct exposure of the aquatic species to dyes and their metabolites, which are toxic, mutagenic or carcinogenic. Azo dyes are the most important class of dyes in textile industry, which account for more than half yield of the

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commercial dyes. Azo dyes are resistant to biodegradation under aerobic condition and toxic to aquatic lives (Banat et al., 1996; Lin and Peng, 1996; Seshadri et al., 1994). Anthraquinone dyes are the second most important class of dyes. They are renowned for the outstanding fastness properties, especially to light (Gordon and Gregory, 1987). Due to the poor biodegradability of most synthetic dyes, it is not always practical to treat dyeing or textile wastewater with the conventional activated sludge process. As an alternative, advanced oxidation processes (AOPs) have attracted wide interests for the treatment of bio-refractory contaminants (Andreozzi et al., 1999; Zhou and Smith, 2001). However, the main problem with AOPs is the high cost (Fernandez-Alba et al., 2002), which constitutes the main obstacle to their commercial application. To overcome this bottleneck, researchers have proposed several promising cost-cutting approaches, such as the combination of AOPs with biological treatment (Parra et al., 2000; Pulgarin et al., 1999; Sarria et al., 2002). Once the biodegradability of the effluent was improved by AOPs, the effluent could then be cost-efficiently treated with bio-process. The key of this foregoing approach is to select the appropriate activating agent in the AOPs.

Some hydroxyl radical based AOPs, such as Fenton reactions, UV/H_2O_2, and UV/TiO_2 systems, have shown potential in dyeing wastewater treatment (Hai et al., 2007; Wang and Xu, 2012). However, the chemicals used in these AOPs are normally toxic to microorganisms or need post-recovery. Some of their degradation products were more toxic than the parent compounds (Padhi, 2012; Weng et al., 2017).

Recently, a method with acetylacetone (AA) as the photoactivator has been developed for dye degradation (Wang et al., 2013; Zhang et al., 2014). The UV/AA process was target-selective to dyes and was more stoichiometrically efficient than the well-known UV/H_2O_2 process. In real dye-containing wastewater, the dye concentration is generally in the range of 40–260 mg L^{-1} (Solís et al., 2012). Because the absorption spectrum of AA has some overlap with that of solar radiation, addition of a low dose of AA (0.25–1 mM) might be sufficient to decolorize dye solutions on sunny days without any other energy input (Wu et al., 2017). AA and its degradation products showed a high bioavailability to the cells in activated sludge (Wu et al., 2016a). Therefore, the UV/AA process might be a promising approach in sequential chemical-biological water treatment. However, so far, there are no experimental evidence on the practicability of the UV/AA process as a pre-treatment step for a further bio-treatment with activated sludge. On the other hand, toxicity assessment and environment impact are crucial for the practical use of a new technology. To the best of our knowledge, the environmental implications of the UV/AA process are unknown.

To close the gap between the known fundamental chemistry of the UV/AA process and its practical use, the main focus of this work was the assessment of the biodegradability and toxicity of the UV/AA treated solutions. Two dye solutions (one azo dye and one anthraquinone dye) were treated with the UV/AA process to various extents and were subjected to toxicity assessment and environment impact. The ratio of 5-day biological oxygen demand (BOD_5) to chemical oxygen demand (COD) and a 28-day activated sludge assay (Zahn-Wellens tests) were employed to evaluate the biodegradability. Toxicity tests were conducted by monitoring the response of organisms (microorganisms in the sludge, *Daphnia magna*, primarily crop plants, terrestrial plants) to the treated solutions. These results are helpful for us to determine whether the UV/AA process is applicable to certain wastewaters and how the UV/AA process could be effectively combined into a sequential chemical-biological water treatment.

2. Materials and methods

2.1. Materials

AA and 30% (V/V) H_2O_2 of analytical grade were purchased and used as received. Ethanol (CH_3OH), aniline (C_6H_7N), potassium dichromate ($K_2Cr_2O_7$), ammonium ferrous sulfate ($(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$), mercury sulfate ($HgSO_4$), silver sulfate ($Ag_2SO_4$), sulfuric acid ($H_2SO_4$), hydrochloric acid (HCl), magnesium sulfate ($MgSO_4$), calcium chloride ($CaCl_2$), cupric chloride ($CuCl_2$), ammonium chloride (NH_4Cl), potassium dihydrogen phosphate (KH_2PO_4), potassium hydrogen phosphate (K_2HPO_4), titanium oxalate ($K_2TiO(C_2O_4)_2$), and sodium hydroxide (NaOH) were all analytical purity grade. Glucose ($C_6H_{12}O_6$) and glutamic acid ($C_5H_9NO_4$) were guaranteed reagent. They were purchased from Nanjing Chemical Reagent (Nanjing, China). Acid Orange 7 (AO7, $C_{16}H_{11}N_2OSO_3Na$) and Reactive Blue 19 (RB19, $C_{22}H_{16}N_2Na_2O_{11}S_3$) were purchased from Sigma-Aldrich (Saint Louis, USA). The purity of AO7 and RB19 are more than 85% and 50%, respectively. LIVE/DEAD™ BacLight™ Bacterial Viability Kit was bought from Thermo Fisher Scientific (Waltham, USA). Ultrapure water was used for the preparation of all sample solutions.

2.2. Irradiation experiments

The irradiation experiments were conducted with a rotary disk photoreactor (Nanjing Stone Tech Electric Equipment, Nanjing, China) and a 300 W medium-pressure mercury lamp. More details about the setup and the light source are available in our previous reports (Liu et al., 2014; Wu et al., 2016a).

2.3. Analytical methods

Dye concentration was detected with a double beam spectrophotometer (Shimadzu UV-2700, Kyoto, Japan). The concentration of AA was analyzed with a Dionex Ultimate 3000 high-performance liquid chromatography (HPLC) system equipped with an UV detector. More details about the eluent compositions and procedures for the HPLC analysis of AA are available in a previous report (Wu et al., 2015). The concentration of H_2O_2 was determined by spectrophotometric method with titanium potassium oxalate (Sellers, 1980). The dissolved organic carbon (DOC) and total organic carbon (TOC) was determined with a TOC-LCSH analyzer (Shimadzu, Kyoto, Japan). The COD was determined with the HACH DRB 200 digester (Hach, Loveland, American) and titrimetric method. The BOD_5 was determined by incubating diluted and seeded solution samples for five days and measuring the loss of oxygen from the beginning to the end of the test. The pH of solution was measured with a FE20K pH meter (Mettler Toledo, Zurich, Switzerland). Degradation products were identified with a Thermo Fisher Scientific Q Exactive™ Focus Orbitrap LC-MS/MS system (Wu et al., 2016b).

2.4. Zahn-Wellens test

The Zahn-Wellens test was carried out according to OECD guideline of testing of chemicals (Wilhelm and Maibach, 2012). A mixture containing the test substance, mineral nutrients and activated sludge in aqueous medium was agitated and aerated at 20–25 °C in the dark or in diffuse light for up to 28 d. Blank controls containing activated sludge and mineral nutrients but no test substance were conducted in parallel. The biodegradation process was monitored by the determination of DOC in filtered samples taken daily or at a certain time interval. The ratio of eliminated DOC, corrected by the blank, to the initial DOC value was referred to the