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Accelerating biodegradation of a monoazo dye Acid Orange 7 by using its endogenous electron donors

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HIGHLIGHTS

- We use endogenous electron donors to accelerate biodegradation of azo dye AO7.
- Sulfanilic and aniline were proved to be the main endogenous electron donors.
- The electron donors accelerated AO7 degradation by driving dioxygenation.

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ABSTRACT

Biodegradation of a monoazo dye – Acid Orange 7 (AO7) was investigated by using an internal circulation baffled biofilm reactor. For accelerating AO7 biodegradation, endogenous electron donors produced from AO7 by UV photolysis were added into the reactor. The result shows that AO7 removal rate can be accelerated by using its endogenous electron donors, such as sulfanilic and aniline. When initial AO7 concentration was 13.6 mg/L, electron donors generated by 8 h UV photolysis were added into the same system. The biodegradation rate 0.4 $mg^{0.05}$ h^{-1} was enhanced 60% than that without adding electron donor. Furthermore, sulfanilic and aniline were found to be the main endogenous electron carriers, which could accelerate the steps of the azo dye biodegradation.

1. Introduction

Global production of dyestuffs has exceeded one million tons, in which azo dyes account for about 70% [1]. Azo dyes contain one or more nitrogen-nitrogen double bond (R-N=N-R'). Benzene, naphthalene and other aromatic compounds are often connected by the nitrogen atoms. In addition, azo dye was proved to be a class of typical refractory organics [2–4]. Nowadays, the most popular treatment for dyeing wastewater is combination of anaerobic hydrolysis acidification and aerobic biodegradation. Anaerobic microorganisms can break the nitrogen-nitrogen double bond by reductive cleavage to generate primary intermediates including aromatic amines [5–7]. Then, the primary intermediates are oxidized by aerobic microorganisms. However, aromatic amines generated by anaerobic degradation of azo dyes have been proven to be carcinogenic and mutagenic [8,9]. Some azo dyes such as Reactive Black 5 and Reactive Violet 5 whose intermediates could not be used by aerobic microorganisms efficiently [10]. This makes decline of azo dye biodegradation rate significantly, leading to effluent of dyeing wastewater still has potential of carcinogenic and mutagenic after biological treatment [11]. Therefore, it is necessary to accelerate biodegradation rate of azo dyes in order to ensure dyeing wastewater treatment effect.

For many refractory organics, the limiting step in their biodegradation is initial rate [12]. The initial rate could be accelerated by a mono-oxygenase/di-oxygenase. This process also requires two co-substrates: molecular oxygen (O_2) and intercellular electron carrier, such as reduced nicotinamide adenine dinucleotide NADH + H^+. As a rule, slow biodegradation process of refractory organics can be accelerated by enhancing concentration of

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mono-oxygenase/di-oxygenase and/or any co-substrate. Furthermore, mono-oxygenation/di-oxygenation reaction was an effective way to accelerate biodegradation process of refractory pollutants [13–16]. Under oxygen-rich conditions, once microorganism obtains sufficient supply of electrons, mostly refractory bioconversion will get quick start by mono-oxygenation/di-oxygenation. Aerobic degradation of an azo dye – Acid Orange 7 in a vertical-flow constructed wetland was reported by Davies et al. [17] Bi-oxygenation played a key role in the azo dye biodegradation. Dihydroxylated compounds such as 4-sulfocatechol or catechol formed during the reaction, which were substrates for cleavage of the aromatic ring, and then broken down into easy degradable components. Microbes gain carbon and electron following the components oxidation. On the other hand, effective electron donor is also a prerequisite for azo dyes biodegradation [10]. The traditional strategy is to apply readily biodegradable carbon source such as glucose or redox mediator into the wastewater [18]. This method is effective, but increases operating costs. Can electron donor be recovered from azo dye itself, then use this part of electron to accelerate azo dye biodegradation? Theoretically, if azo dye can generate biodegradable intermediates after a certain pretreatment, the intermediates can be used as primary substrates (containing readily biodegradable chemical oxygen demand) to provide effective electron for azo dyes biodegradation. In addition, increase of primary substrate concentration will improve the rate of mono-oxygenation/di-oxygenation reaction, then accelerate the slow biodegradation process of azo dyes. Importantly, some intermediates of azo dyes have been shown to be good electron carriers [19].

To the best of our knowledge, the mechanism of accelerating azo dye biodegradation by using endogenous electron donors has not been reported in the literature. The main focus of the present work is to evaluate whether we can use intermediates as endogenous electron donors for accelerating azo dyes biodegradation. To reveal the mechanism, UV radiation was chosen to be the pretreatment of a monoazo dye–Acid Orange 7 (AO7) in this work. AO7 was chosen as a model contaminant, since it is difficult to be biodegraded and is widely used in the textile, food, and cosmetics industries [20–22].

2. Materials and methods

2.1. Chemicals and AO7 solutions

AO7, sulfanilic acid (SA) and aniline (AN) of analytical grade were purchased from Shanghai Reagent Station. All reagents and chemicals were used without further purification. All samples were prepared in ultrapure deionized water (18 MΩ, prepared with MILLIPORE (USA) water purifier).

AO7 was added to ultrapure deionized water to obtain a 1000 mg/L stock solution, and AO7 solutions for specific experiments were diluted with ultrapure deionized water to get different initial concentrations according to the need for the radiation or biodegradation experiment.

2.2. UV radiation of AO7 solution

To evaluate photolysis of AO7, the solution was placed in a glass dish with a water depth of 2 cm. The content was mixed with an air pump system (ACO-5501, Hailea) and illuminated by UV light with a wavelength of 253.7 nm (UV-C range, Philips), power of 24 W. Light intensity was controlled by the distance between UV lamps and water surface by a lifting platform, and was measured by a UV light meter with a UV-C probe (BG-2254, UV LIGHT MRTER). Water samples were taken at regular intervals to measure AO7 and its photolytic products.

2.3. Bioreactor and biofilm formation

An internal circulation baffled biofilm reactor (ICBBR), similar to the one used by Zhang et al. [16], was employed for AO7 biodegradation. The ICBBR, which had a total liquid volume of 800 mL, was divided into top and bottom sections by a segregation board. Twelve ceramic porous plates were installed in the bottom section of reactor with staggered levels to create serpentine flowing through the lower baffled biofilm section. The liquid medium was driven by a pump to circulate continuously at 400 L/h between the upper oxygen rich section and the lower biodegradation section. The flow rate gave 500 cycles per hour.

Acclimated activated sludge was fed into the reactor to immerse the ceramic plates and form a preliminary biofilm by adsorption. The biofilm was then acclimated with daily batch feeding of a solution containing 20 mg/L AO7 and 200 mg/L glucose for 14 days, during which culture solution was replaced every day by fresh culture medium until 20 mg/L of AO7 was fully removed within 10 h. After biofilm formation, glucose was not added into ICBBR during AO7 biodegradation experiments.

2.4. AO7 biodegradation experiments

All AO7 biodegradation experiments were carried out in batch. During all experiments, samples were taken at time intervals to measure the concentrations of AO7, its intermediates, and other indexes. **The first set of experiments was to identify the effects from the all photolysis products followed two protocols**: biodegradation alone (B) and biodegradation after photolysis (P + B). For P + B, an AO7 solution with an initial concentrations of 20 mg/L was first illuminated with UV light for 4 h or 8 h to get final AO7 concentrations of 13.6 mg/L or 11.6 mg/L, and that solution was then subjected to biodegradation in the ICBBR. For B, the experiments were carried out in the ICBBR with an AO7 concentration of 13.6 mg/L or 11.6 mg/L. **The second set of experiments was to identify the effects from the main photolysis products**. Experiments were carried out with the protocol P + B, and biodegradation after main intermediates addition (I + B). For P + B, an AO7 solution with an initial concentration of 20 mg/L was first illuminated with UV light for 5 h to get final AO7 concentrations. For I + B, AO7 supplemented with UV main photolysis products sulfanilic acid (SA) and aniline (AN). The concentrations of the two products were same to the generation contents after 5 h photolysis of 20 mg/L AO7. In addition, AO7 concentrations of ICBBR influent of the two experiments were both 13.9 ± 0.76 mg/L. The third set of experiments was carried out with the protocol I + B. **The third set was to identify the acceleration effect of the two electron donors – SA + B and AN + B, respectively**. The protocols of SA + B and AN + B shared the same experiment conditions.

2.5. Analytical methods

AO7 concentration was analyzed by using a UV–vis spectrophotometer (UV-2550, Shimadzu, Japan). The UV–vis spectra (190–900 nm) were recorded and dye concentration calculated at λ_{max} (483 nm). SA and AN were measured with a high performance liquid chromatograph (HPLC, model: 1100, Agilent, U.S.) equipped with a diode array detector (DAD) with wavelength of 205 nm and ZORBAX SB-C18 column (5 μm, 4.6 × 150 mm, Agilent, U.S.). For SA, the mobile phase was 0.1 mol/L ammonium dihydrogen phosphate, and the flow rate was 1 mL/min. For AN, the mobile phase consisted of methanol and ultra-pure water with a ratio of 70:30 (v/v) and at a flow rate of 1.0 mL/min. All samples were filtrated with 0.22 μm membrane before measurement. DO, pH and temperature were measured by microprocessor meters (HQ30D, HACH, U.S.).