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Fe^0 catalyzed photo-Fenton process to detoxify the biodegraded products of azo dye Mordant Yellow 10

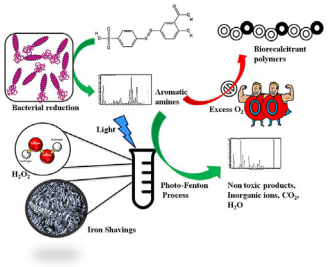
R. Brindha, P. Muthuselvam, S. Senthilkumar, P. Rajaguru*

Department of Biotechnology, Bharathidasan Institute of Technology, Anna University, Tiruchirappalli, 620 024, Tamilnadu, India

HIGHLIGHTS

- Fe^0 catalyzed photo-Fenton approach was employed as secondary treatment for azo dye degradation.
- Monoazo dye MY10 was degraded into aromatic amines in primary anaerobic bacterial treatment.
- Aromatic amines were mineralized in photo-Fenton oxidation.
- Plausible degradation routes of the integrated sequential approach were elucidated.
- Detoxification efficiency of Fe^0 catalyzed photo-Fenton approach was revealed.

GRAPHICAL ABSTRACT



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ABSTRACT

Inspired by the efficiency of the photo-Fenton process on oxidation of organic pollutants, we herein present the feasibility of visible light driven photo-Fenton process as a post treatment of biological method for the effective degradation and detoxification of monoazo dye Mordant Yellow 10 (MY10). Anaerobic degradation of MY10 by *Pseudomonas aeroginosa* formed aromatic amines which were further degraded in the subsequent Fe catalyzed photo-Fenton process carried out at pH 3.0, with iron shavings and H_2O_2 under blue LED light illumination. LC-MS and stoichiometric analysis confirmed that reductive azo bond cleavage was the major reaction in anaerobic bacterial degradation of MY10 producing 4-amino benzene sulfonic acid (4-ABS) and 5-amino salicylic acid (5-ASA) which were further degraded into hydroxyl amines, nitroso and di/tri carboxylic acids by the photo-Fenton process. Toxicity studies with human small cell lung cancer A549 cells provide evidence that incorporation of Fe^0 catalyzed photo-Fenton step after anaerobic bacterial treatment improved the mineralization and detoxification of MY10 dye.

1. Introduction

The growing impact of environmental concern promotes lesser consumption of water and lowers output of wastewater. However, the discharge of effluents with synthetic dyes is still very problematic. Physico-chemical characteristics of chemical loaded textile effluent severely restrict the choice of microorganisms for the biological treatment, as they require highly tolerant cultures, making most of the conventional treatment procedures unsuitable (Ogugbue and Sawidis, 2011). Even though decolorization of azo dyes is easily accomplished by bacterial strains under anaerobic

* Corresponding author.
E-mail address: rajaguru62@gmail.com (P. Rajaguru).

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conditions, the biotransformation of toxic aromatic amine containing metabolites into non-toxic compounds in aerobic process is extremely challenging as excess oxygen leads to polymerization of aromatic amines and the complete degradation cannot be guaranteed for all the aromatic amines. In addition, the unpredictable nature of the bacterial action against azo dyes pretense the varying toxicity of metabolites and its susceptibility towards further degradation. Hence secondary treatment is very crucial for the microbe mediated dye degradation to combat environmental toxicity.

Several studies discussed the combination of advanced oxidation processes (AOP) and biological treatment (Sarria et al., 2002; García-Montaño et al., 2008; Wang et al., 2017). By assessing the cost effectiveness of different AOPs, photo-Fenton process is much preferred (Azbar et al., 2004), especially under visible light irradiation. Integrating it with the biological method significantly reduces the chemical dosage and thereby the operating cost. In integrated treatment systems for degrading azo dyes, photo-Fenton was either employed as chemical pre-treatment or post-treatment of biological method. In the former approach, Fenton process cleaves the recalcitrant azo structures to biodegradable intermediates (García-Montaño et al., 2006; Kiran et al., 2013), whereas in latter approach it mineralizes the aromatic amines that are formed during the anaerobic degradation of azo compounds using Ferrous ion solutions as catalyst (Jonstrup et al., 2011; Punzi et al., 2015). Though the efficiency of integrated photo-Fenton/aerobic process is higher, high chemical (H_2O_2 and Fe^{2+}) requirement to increase the biodegradability of azo dyes, negative effects of residual H_2O_2 on microorganisms (Wang et al., 2017) and uncertainty of complete mineralization of aromatic amines and other intermediates in biological methods limits its application in real textile wastewater treatment (Bisschops and Spanjers, 2003). Recently, the use of higher loads of iron in Fenton process was questioned while iron acts as catalyst alone, and hence efforts have been steered toward reagent dosage reduction with regard to legal limits for iron disposal. Realizing this, we conducted the study to analyze the feasibility of biological/photo-Fenton treatment using salt tolerant bacteria and zerovalent iron (shavings) for the degradation of azo dye, Mordant Yellow 10.

2. Materials and methods

2.1. Materials

Mordant Yellow 10 (MY10) (CAS: 6054-99-5; $C_{13}H_8N_2Na_2O_6S$; MW 366.26; λ_{max} 354 nm) was purchased from Acros Organics (Thermo Fisher Scientific, USA) and used as received without further purification. Sulphanilic acid (CAS: 121-57-3; $C_6H_7NO_3S$; MW 173.19) and 5-amino salicylic acid (CAS: 89-57-6; $C_7H_7NO_3$; MW 153) were purchased from Tokyo Chemical Industry Co Ltd, Japan. All other chemicals were purchased from Himedia Laboratories, Mumbai unless otherwise indicated. The dye stock solution (10 mg mL^{-1}) was prepared in distilled water and filter sterilized (GS 0.22 μm filter, Millipore Millex®). Minimal salt medium (MSM, pH 7.0 ± 0.1) was formulated with the following composition (in g L^{-1}): K_2HPO_4-0.2; $MgCl_2$-0.08; $CaCl_2$-0.02; NaCl-1.0. MSM was further supplemented with 100 mg L^{-1} (0.273 mM) of MY10 as sole substrate and 10.0 g L^{-1} of glucose as the co-substrate. Twisted iron shavings obtained from a lathe industry were treated with 3% HCl for 30 min on a shaker at 150 rpm, washed with distilled water followed by acetone wash and then stored in a glass bottle. Human small cell lung carcinoma (A549) cells were obtained from NCCS (National Centre for Cell Science, Pune, India) and cultured in DMEM (GIBCO, Invitrogen, USA), supplemented with 10% heat inactivated FBS, 2 mM L-glutamine (GIBCO, Invitrogen, USA) and 100 U mL^{-1} penicillin-streptomycin (GIBCO, Invitrogen, USA).

2.2. Anaerobic microbial degradation

The halotolerant strain of *Pseudomonas aeroginosa* BRPO3 isolated from marine coastal soil was acclimatized through exposure to increasing concentration of MY10 dye and NaCl. MSM containing 100 mg L^{-1} (0.273 mM) of MY10 was inoculated with 1% of the overnight grown cultures (LB medium, at 37 °C for 12 h) of *P. aeroginosa* BRPO3 and incubated in static anoxic condition at 37 °C until complete disappearance of color. Culture samples were withdrawn periodically and centrifuged at 8000 rpm for 15 min at 4 °C. The cell free supernatant was analyzed for color intensity at the λ_{max} of MY10 (350 nm) using UV–Vis spectrophotometer (Thermo Scientific BioMate 3S), aromatic amine using the modified method of Bratton Marshal Assay (Pielesz et al., 2002), protein by the method of Lowry et al. (1951), glucose using DNSA method (Miller, 1959) and for extracellular enzymes as described below. The cell pellets were resuspended in 50 mM phosphate buffer (pH 7.0), and sonicated by giving 10 strokes of 30 s each for 2 min interval based on 60 amplitude output at 4 °C (Sonics-vibracell ultrasonic processor). These cells were further centrifuged at 8000 rpm for 15 min at 4 °C and the supernatant was used as the source of intracellular enzymes. Intra- and extra cellular enzyme activities of NADH and FAD dependent azoreductase, laccase and NADH dependent DCIP reductase were determined by the protocols suggested by Zimmermann et al. (1982), Arora and Sandhu (1985) and Salokhe and Govindwar (1999), respectively.

2.3. Photo-Fenton oxidation

The microbially decolorized solutions of MY10 were further subjected for photo-Fenton oxidation. A 30 mL portion of the decolorized solution taken in 50 mL transparent polypropylene tubes was acidified to pH 3.0 with 1 M HCl and added with different dosages of iron shavings (10, 20, 40, 80, and 160 mg). Split doses of H_2O_2 (100, 200, 400, and 1000 mM) were added to initiate the process. The tubes were irradiated with two LED Blue lamps (0.5 W Philips) placed on either side at 8 cm distance and stirred at 30 rpm using a rocking table. A similar set up was followed without pH adjustment. Samples were withdrawn for every 10 min interval from which a portion was assayed for ferrous and ferric concentration using ammonium thiocyanate and 1,10-phenanthroline method (APHA, 1998). Remaining portion was added with quenching solution (0.1 M Na_2SO_3, 0.1 M NaOH, 0.1 M KI) in the ratio of 1:2.5, centrifuged at 8000 rpm for 15 min and the supernatant was assayed for residual aromatic amine using Bratton Marshal method (Pielesz et al., 2002). The decolorization efficiency of photo-Fenton process using iron shavings as a standalone treatment was evaluated with 50 and 100 mg L^{-1} of MY10 at different operational conditions.

2.4. Characterization of iron shavings

Surface charge of iron shavings (C mm^{-2}) in 100 mg L^{-1} of MY10 solution and bacteria decolorized solution were determined at different pH (2, 3, 4.5, 7 and 10) using potentiometric titration method as described in Xiong and Peng (2008). Terephthalic acid (0.5 mM in 2 mM NaOH) was used as fluorescence probe to detect the •OH radicals generated from H_2O_2 (Yu et al., 2009). Experiments were conducted as explained in section 2.3 replacing the microbially decolorized dye solution with terephthalic acid. Doses of H_2O_2 were added with continuous visible light irradiation. Samples were withdrawn for every 10 min and the photoluminescence spectra was measured using multi mode detector (Spectramax M3,