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Research article

Influence of redox mediators and salinity level on the (bio) transformation of Direct Blue 71: kinetics aspects

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ABSTRACT

The rate-limiting step of azo dye decolorization was elucidated by exploring the microbial reduction of a model quinone and the chemical decolorization by previously reduced quinone at different salinity conditions (2–8%). Microbial experiments were performed in batch with a marine consortium. The decolorization of Direct Blue 71 (DB71) by the marine consortium at 2% salinity, mediated with anthraquinone-2,6-disulfonate (AQDS), showed the highest rate of decolorization as compared with those obtained with riboflavin, and two samples of humic acids. Moreover, the incubations at different salinity conditions (0–8%) performed with AQDS showed that the highest rate of decolorization of DB71 by the marine consortium occurred at 2% and 4% salinity. In addition, the highest microbial reduction rate of AQDS occurred in incubations at 0%, 2%, and 4% of salinity. The chemical reduction of DB71 by reduced AQDS occurred in two stages and proceeded faster at 4% and 6% salinity. The results indicate that the rate-limiting step during azo decolorization was the microbial reduction of AQDS.

1. Introduction

Wastewater from textile industries contains a huge number of pollutants. Azo dyes are one of the main compounds, representing 60–70% of all textile dyes used worldwide and thus are associated with several environmental and human health concerns. The concentration of azo dyes in wastewater typically is in the range of 10–200 mg L^{-1} (O'Neill et al., 1999), which is undesirable not only for the color provided, but also for its contribution to pollution in terms of chemical oxygen demand (COD, 150–10,000 mg L^{-1}) and biological oxygen demand (BOD, 100–4000 mg L^{-1}) (Kalra et al., 2011).

Azo dyes are electron accepting contaminants and remain unaffected during conventional aerobic wastewater treatment; however, these compounds are susceptible to redox biotransformations under anaerobic conditions (Field et al., 1995). Nonetheless, the biotransformation of electron accepting contaminants occurs very slowly due to electron transfer limitations and toxicity effects, leading to poor performance or even collapse of anaerobic bioreactors (Rodgers and Bunce, 2001; van der Zee et al., 2001). For the past 20 years, evidences have been accumulated indicating that humic substances (HS) and quinoid analogues can act as redox mediators (RM) during the reductive biodecolorization of azo dyes (Barkovskii and Adriaens, 1998; Guo et al., 2007), accelerating redox reactions several orders of magnitude. In some cases RM are essential for reactions to take place (Van der Zee and Cervantes, 2009).

In spite of the advantages of using RM in a decolorization process, their application at real scale depends on some aspects such as cost-effective sources of HS with redox active groups, immobilization in a suitable support to prevent continuous dosage, engineering of HS (Van der Zee and Cervantes, 2009), and wastewater characteristics (such as salinity level). Wastewater from textile industries contains high levels of salinity (in some cases up to 20%), and most of the biological decolorization studies using RM have been carried out under non-saline conditions with anaerobic granular sludge not adapted to salinity. Microorganisms can be physiologically affected (e.g. decreasing or inhibition of methanogenesis) under moderated salinity conditions (Lefebvre et al.,

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2007), requiring gradual adaptation by increments of salt concentration (Gebauer, 2004; Rao et al., 2005), which is a time-consuming step. These concerns suggest that the role of non-halotolerant microorganisms could be unsuitable to be employed for wastewater treatment systems of textile industries containing high levels of salinity. On the other hand salinity adapted microorganisms could represent a safer alternative to treat effluents containing azo dyes. There are many published studies dealing with the use of pure cultures of halotolerant or halophilic microorganisms in a decolorization process (Amoozegar et al., 2011). Nevertheless, the use of halotolerant-microbial consortia with quinones or HS as RM is scarce in the literature. Recently was reported the use of three pure strains of *Shewanella* (*algae, aquimarina,* and *marisflavi*) for decolorization using different redox mediators and saline conditions (Meng et al., 2014). These authors documented that the three *Shewanella* strains used quinones and HS as electron acceptors to support their growth in the presence of 0–7% of salinity, but important aspects as the effect of different salt concentrations during the biotransformation mediated by RM and the chemical reduction of dyes were not considered.

A biodecolorization process of azo dyes mediated by HS or model quinone occurs in two steps as illustrated in Fig. 1. The first step is conducted by the humus-reducing microorganisms using an organic substrate as energy sources and HS or quinones as electron acceptor. Then, in the second step, RM donates their electrons to promote the reduction of electron-accepting contaminants such as azo dyes. The objectives of the present work are: 1) to assess the impact of different salt concentrations on the rate of microbial decolorization of azo dye mediated by HS and quinones; namely, the entire process (step 1 and 2 simultaneously); and 2) to evaluate the rate of microbial reduction of a model quinone (step 1), and the rate of chemical decolorization of azo dye by previously reduced quinone (step 2), at different salinity conditions.

2. Materials and methods

2.1. Reagents

Anthraquinone-2,6-disulfonate (AQDS) and riboflavin (RB), both from Sigma Aldrich, were selected as model RM. Humic acid leonardite (HAL) from the International Humic Acid Society (IHSS No. 1BS104L) and Humic acid sodium salt (HASS) from Sigma Aldrich (H16752) were also used as RM. DB71 was selected as the model azo compound (Sigma Aldrich, 40% of purity). All compounds were used without further purification.

2.2. Marine consortium and batch assay conditions

The marine consortium was prepared from a sediment collected in the coastal zone located in "Bahía de Lobos" Sonora, Mexico. The sediment was extracted from a discrete depth of 10 cm, and preserved at 4.0 °C prior to be used. Microorganisms were isolated from the sediment by using the commercial saline mediums Halovivax, Natronobacter, and Marine Broth, following the serial dilution technique (10^{-1}–10^{-6}) and streak in plates. The identified colonies were isolated and re-cultured in the same saline medium. The twenty-one isolated microorganisms were grown and preserved in agar marine medium (DIFCO) and marine broth (DIFCO) at 37 °C and 2% of salinity. The isolated microorganisms were morphologically and biochemically characterized by using classical tools of microbiology (Meza-Escalante et al., 2012).

The marine consortium was prepared with the twenty-one isolated strains, and subsequently inoculated in a lab-scale (0.8 L) up-flow anaerobic sludge blanket reactor (UASB) at 5 g of volatile suspended solids (VSS) L^{-1} with a hydraulic residence time (HRT) of 24 h to be acclimatized. The reactor was feed with glucose as a sole energy source at 1 g of COD L^{-1}, 1% of salinity (NaCl), and was maintained at room temperature (~25 °C). The basal medium was prepared as follows (g L^{-1}): KH_2PO_4 (0.6); $MgCl_2 \cdot 6H_2O$ (0.2); K_2HPO_4 (1.6); $NaSO_4$ (1.0); and 1 mL of trace element solution composed of (g L^{-1}): $FeCl_3$ (0.03); $CaCl_2$ (0.6); $CuSO_4 \cdot 5H_2O$ (0.02); and $NaMoO_4 \cdot 2H_2O$ (0.12), which was previously described by Meza-Escalante et al. (2012). The marine consortium was used in batch assays until the reactor showed stable removal efficiencies in terms of COD, which was >90% after two months of continuous operation.

Batch assays were conducted in duplicate in serum bottles of 120 mL. The basal medium for a total volume of 50 mL were dispensed in the bottles, which were then sealed with rubber stoppers and aluminum caps. The atmosphere in the headspace (70 mL) was replaced with helium (He) in order to create anaerobic conditions. For microbial incubations, the marine consortium was twice washed with 0.9% NaCl solution. Then, the bottles were inoculated with 1 g VSS L^{-1}, and supplied with 1 g COD L^{-1} of glucose. All bottles (microbial and chemical incubations) were incubated at 30 °C and 200 rpm.

2.3. Microbial decolorization of DB71 in presence of different RM

The catalytic capacity of AQDS (1 mM), RB (1 mM), HAL (200 mg L^{-1}), and HASS (200 mg L^{-1}) was evaluated during the

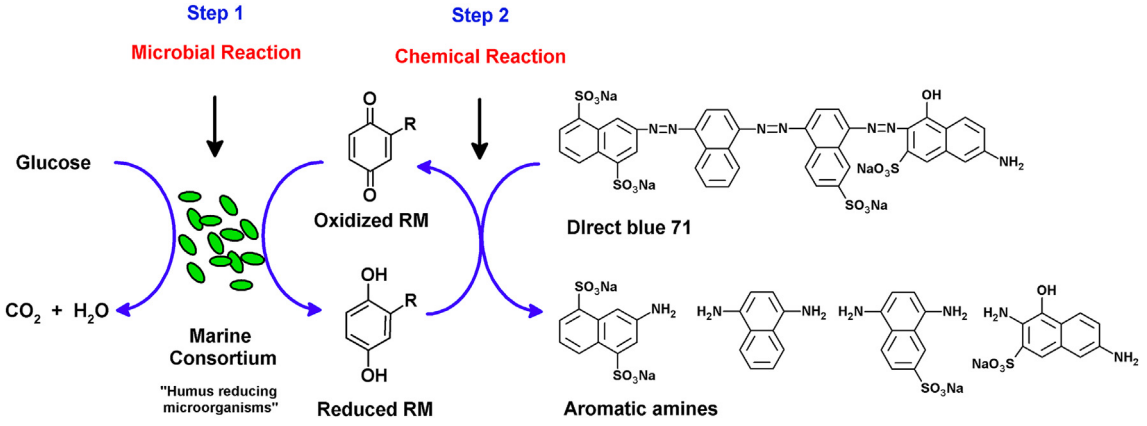

Fig. 1. Biodecolorization of Direct Blue 71. The first step is conducted by humus-reducing microorganisms using HS or quinones as electron acceptor. In the second step, the redox mediator donates electrons for reduction of azo dye.