PROCESS BIOCHEMISTRY

Process Biochemistry 40 (2005) 35–44

www.elsevier.com/locate/procbio

# Reactor performances and fate of aromatic amines through decolorization of Direct Black 38 dye under anaerobic/aerobic sequentials

Delia Teresa Sponza*, Mustafa Işık

*Environmental Engineering Department, Engineering Faculty, Dokuz Eylul University, Buca Kaynaklar Campus 35160, Izmir, Turkey*

Received 29 November 2002; received in revised form 13 November 2003; accepted 22 November 2003

**Abstract**

The removal of aromatic amines was evaluated by decolorization of CI Direct Black 38 (DB 38) dye varying between 100 and 3200 mg $l^{-1}$ using an anaerobic upflow anaerobic sludge blanket reactor and an aerobic completely stirred tank reactor system. The effect of increasing dye loadings from 6.1 to 213.0 g $m^{-3}$ $h^{-1}$ on decolorization and COD removal efficiency was investigated at constant glucose-COD (2000 mg $l^{-1}$) concentrations in an UASB reactor. For 3200 mg $l^{-1}$ of DB 38 and 2000 mg $l^{-1}$ glucose-COD as co-substrate in the feed, 48.4% COD and 80% color removal efficiencies were observed at a maximum COD and dye loading rates of 5.37 kg COD $m^{-3}$ per day and 213 g dye $m^{-3}$ $h^{-1}$, respectively at a hydraulic retention time (HRT) of 15 h in the UASB reactor. Sixty seven percentage remaining COD was removed at an HRT of 2.3 days and a maximum organic loading rate of 0.77 kg COD $m^{-3}$ per day in the aerobic stage. Eighty four percentage COD, 86% color and 52.2% total aromatic amine (TAA) was removed at an HRT of 2.9 days and at an organic loading rate of 1.17 kg COD $m^{-3}$ per day and a maximum DB 38 dye loading rate of 46.4 g dye $m^{-3}$ $h^{-1}$, respectively in a total system treating 3200 mg $l^{-1}$ CI Direct Black 38 dye. The TAA produced under anaerobic conditions was ultimately removed in the aerobic stage and aromatic amine recoveries such as 45–50% were obtained in the aerobic reactor. The anaerobic/aerobic sequential process provides simultaneous color, COD and carcinogenic amine removal.


*Keywords:* Azo dye; Aromatic amine; CI Direct Black 38; Anaerobic/aerobic sequential system

## 1. Introduction

Under anaerobic conditions, azo dyes are readily cleaved via a four electron reduction at the azo linkage generating aromatic amines [1–3]. Aromatic amines are considered to be stable biotransformation products of azo dye metabolism by anaerobes. It is generally assumed that aromatic amines derived from azo dyes are not degraded under anaerobic conditions. This observation coupled with the fact that many aromatic amines are completely degraded under aerobic conditions has led to the proposal that anaerobic/aerobic systems might be effective in achieving the complete biodegradation of azo dyes.

Cleavage of the azo bonds generates aromatic amines [4,5] which, with few exceptions [6,7], are not degraded anaerobically [8,9]. Some azo dyes are not normally cytotoxic, mutagenic or carcinogenic but the amines formed by anaerobic digestion may possess these characteristics [10]. Aromatic amines can be mineralized by means of aerobic treatment by non-specific enzymes through hydroxylation and ring opening of the aromatic compounds [11]. Field et al. [12] showed that the aerobic stage of the combined anaerobic/aerobic treatment of dye wastes eliminated the additional COD, attributed to the removal of aromatic amines, which are anaerobically recalcitrant. The complete mineralization of dyes therefore occurs via biodegradation of amines to $CO_2$, $H_2O$ and $NH_3$ under aerobic conditions. As a consequence, anaerobic/aerobic sequential processes could prove effective for the reduction of both color and organic carbon [5,13–17]. Therefore, anaerobic treatment followed by aerobic treatment can be used to decompose putatively toxic and carcinogenic compounds efficiently as reported by some investigators. In a study carried out by Rajaguru et al. [18], it was observed that Congo Red dye, which is a banned azo dye, was treated with a maximum degradation of 134.9 mg $l^{-1}$ per day when the glucose utilization rate was 38.9 mg $g^{-1}$ in a sequential anaerobic/aerobic system.

* Corresponding author. Tel.: +90-232-4531008/1119; fax: +90-232-4531153.

*E-mail addresses:* delya.sponza@deu.edu.tr (D.T. Sponza), mustafa.isik@deu.edu.tr (M. Işık).

0032-9592/$ – see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/j.procbio.2003.11.030

However, O'Connor and Young [19] found that three aromatic amines, 2-aminophenol, 4-aminophenol and 5-aminosalisylic acid (5-ASA), can be mineralized in methanogenic consortia. Kalyuzhnyi et al. [20] reported that 5-ASA did not inhibit methanogenesis up to concentrations of 3–7 mg $l^{-1}$. Donlon et al. [21] found that mordant orange 1 azo dye was reductively cleaved to less toxic aromatic amines (1,4-phenilenediamine and 5-aminosalicylic acid) under anaerobic conditions.

No study had been performed in the past to assess the fates of aromatic amines released through the decolorization of CI Direct Black 38 azo dye. Studies with CI Direct Black 38 are limited with the decolorization study performed by Isýk and Sponza [22]. They reported that benzidine and VFAs were produced as degradation intermediates, through the decolorization of the dye by *Escherichia coli*, *Pseudomonas* sp., demonstrating that aromatic amines were produced as degradation intermediates of dye and glucose. These aromatic amines were not mineralized and accumulated through the anaerobic stage.

In the work presented here, an UASB/CSTR sequential reactor system was used to demonstrate the formation, degradation, removal and recoveries of aromatic amines produced from the cleavage of DB 38 azo dye through decolorization. Furthermore, the effect of increasing dye loadings on methane gas, color, and COD removal was investigated under anaerobic and aerobic conditions.

## 2. Materials and methods

### 2.1. Experimental lab-scale reactors and seed

The anaerobic UASB reactor used for DB 38 decolorization was 6 cm in diameter, 100 cm in length and had an effective volume of 1.32 l). The aerobic CSTR reactor consisted of an aeration tank (effective volume = 9 l) and settler with a volume of 1.32 l. The schematic configuration of the sequential UASB/CSTR reactor is illustrated in Fig. 1. Wastewater passage from the aeration tank to the sedimentation tank was through the holes in the inclined plate and sludge recycle was through the gap under the plate. The effluent of the anaerobic UASB reactor was used as the influent of the aerobic CSTR reactor. Partially granulated anaerobic sludge was used as seed in the UASB reactor and was taken from the methanogenic reactor of Pakmaya Yeast Baker Factory in Izmir. Activated sludge taken from DYO Dye Industry in Izmir was used as seed in the aerobic CSTR.

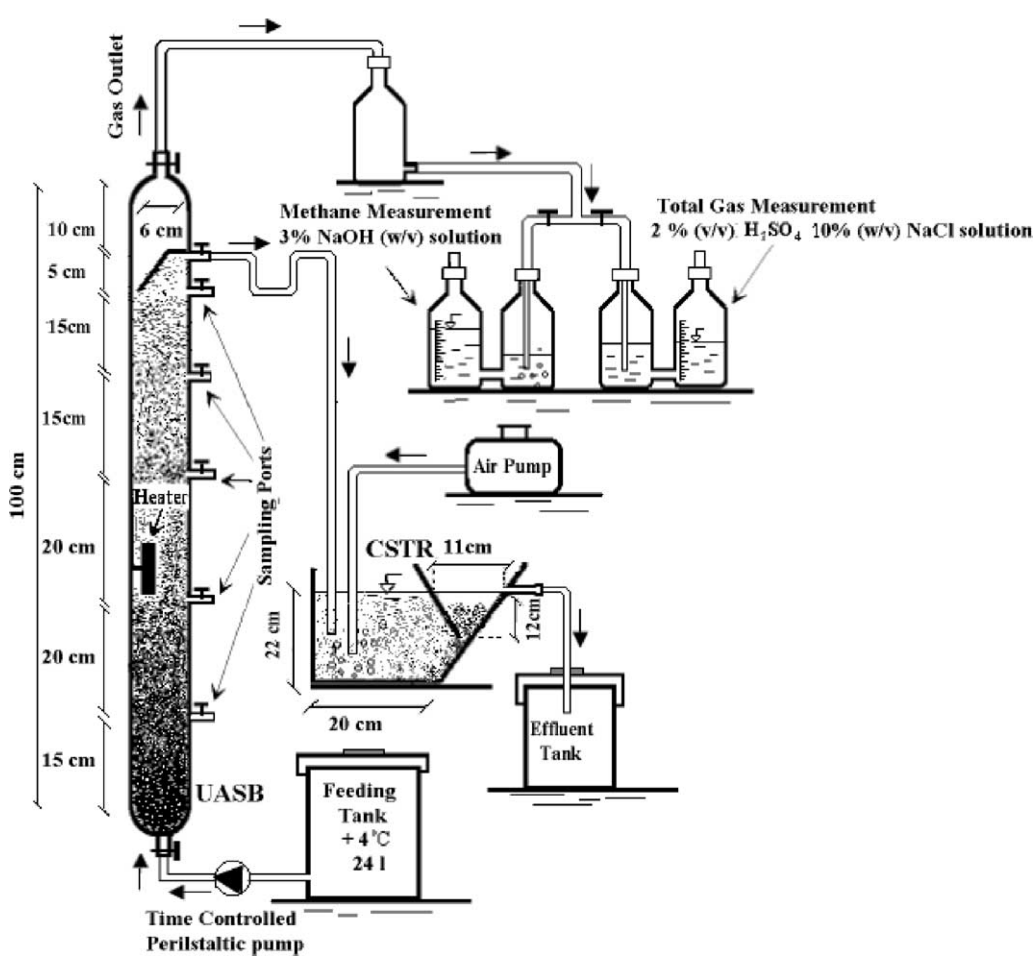


Fig. 1. Schematic configuration of lab-scale anaerobic/aerobic sequential reactor system.