Chemical Engineering Journal 243 (2014) 355–363

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Efficient azo dye removal in bioelectrochemical system and post-aerobic bioreactor: Optimization and characterization

Dan Cui [a], Yu-Qi Guo [b], Hyung-Sool Lee [c], Hao-Yi Cheng [a], Bin Liang [a], Fan-Ying Kong [a], You-Zhao Wang [a], Li-Ping Huang [d], Mei-Ying Xu [e], Ai-Jie Wang [a,*]

[a] State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, No. 202 Haihe Road, Harbin 150090, PR China
[b] The Architecture Design and Research Institute of Harbin Institute of Technology, No.202 Haihe Road, Harbin, 150090, PR China
[c] Department of Civil and Environmental Engineering, University of Waterloo, 200 University Avenue West Waterloo, Ontario N2L 3G1, Canada
[d] Key Laboratory of Industrial Ecology and Environmental Engineering, Ministry of Education (MOE), School of Environmental Science and Technology, Dalian University of Technology, Dalian 116024, PR China
[e] State Key Laboratory of Applied Microbiology, Guangdong Institute of Microbiology, 100 Central Xianlie Road, Guangzhou 510070, PR China

HIGHLIGHTS

- A new refractory wastewater treatment process (UBER–ABOR) was developed.
- Alizarin Yellow R as the mode of azo dyes was efficiently removed.
- The effect of cathode size on the performance of UBER was investigated.
- The HRTs of UBER and ABOR were optimized.
- The degradation mechanism of azo dye was discussed.

ARTICLE INFO

Article history:
Received 18 July 2013
Received in revised form 24 October 2013
Accepted 27 October 2013
Available online 4 November 2013

Keywords:
Up-flow bio-electrocatalyzed electrolysis reactor (UBER)
Cathode size
Hydraulic retention time (HRT)
AYR by-products
Aerobic bio-contact oxidation reactor (ABOR)

ABSTRACT

A new process of an up-flow bio-electrocatalyzed electrolysis reactor (UBER) connected with an aerobic bio-contact oxidation reactor (ABOR) was developed for treating azo dye wastewater. Alizarin Yellow R (AYR), used as a model dye, was efficiently decolorized in UBERs (97.5 ± 1.0%) and further mineralized in the subsequent aerobic bio-contact oxidation reactor (ABOR). Decolorization efficiency was improved with increasing cathode size in UBERs, but AYR removal rate and current density were not increased in proportion to cathode size, mainly due to the limitation of anodic reactions. AYR decolorization rate was optimized at a cathode size of 90 cm^3 in an UBER where the charge transfer resistance R_{ct} (39.5 Ω) was minimal. We assessed the effect of hydraulic retention time (HRT: 6.5 h, 4.5 h, 3.5 h, 2.0 h) on the removal of residual by-products (p-phenylenediamine (PPD) and 5-aminosalicylic acid (5-ASA) in the ABOR. The concentrations of PPD and 5-ASA decreased down to 0.28 ± 0.01 and 0.27 ± 0.03 mg L^{-1}, respectively, in an optimum HRT 3.5 h. Decolorization efficiency and COD removal efficiency was 93.8 ± 0.7% and 93.0 ± 0.5% in the combined process of UBER and ABOR in overall HRT 6 h (HRT 2.5 h in UBER + HRT 3.5 h in ABOR). The Chroma in ABOR effluent was 80 times.

1. Introduction

Azo dyes are the largest chemical class of dyes and are frequently used for textile dying and paper printing industries due to cheap costs, firmness, and a variety of colors compared to natural dyes [1]. However, intensive color of dye-containing wastewater leads to severe aesthetic problems and obstructs light penetration and oxygen transfer into water bodies, adversely affecting aquatic life [2]. For these reasons, the color removal from dye-containing wastewater is one of major concerns in China where textile industry has grown exponentially in recent years [3]. Azo dyes are characterized by the number of azo groups (—N=N—), which was typically recalcitrant to microbial aerobic oxidation but could be reduced easily [4]. The azo group is substituted with benzene or naphthalene groups, which can contain many different substituents, such as chloro (—Cl), methyl (—CH_3), nitro (—NO_2), amino (—NH_2), hydroxyl (—OH), and carboxyl (—COOH). Azo dyes typically remain in tail water after biological wastewater treatment processes because of their recalcitrance; by-products of azo dyes are even toxic and mutagenic [5]. Thus, the complete mineralization of azo dyes into carbon dioxide is desirable to protect ecosystem and human health. A number of removal technologies have been developed, which include dyestuff

* Corresponding author. Tel./fax: +86 451 86282195.
E-mail address: waj0578@hit.edu.cn (A.-J. Wang).

1385-8947/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cej.2013.10.082

adsorption [6,7], electrochemical oxidation or reduction methods [8,9], electrochemical treatment combined with ultrasound technique [10], electrochemical coagulation [11], advanced oxidation [12] and membrane separation processes [13,14]. Each of these techniques offers advantages, but also has limitations, such as significant amounts of chemicals, high operating and maintenance costs, and large amounts of excessive sludge. Biological anaerobic treatment was proposed as an alternative approach to improve the economic efficiency in azo dye wastewaters treatment [15–17]. However, anaerobic treatment is usually very slow (large footprint) and would require exogenous electron donor for reducing azo dye, which can increase investment, and operating and maintenance costs [17,18].

In recent years, bio-electrochemical systems (BESs) have been explored to reduce refractory substances including azo dyes into stable, less toxic forms of aromatic amines in more economical ways because anodic bacteria can oxidize biodegradable fractions of wastewaters as electron donor, deliver them to the anode, and refractory matters could be electrochemically reduced to less toxic forms on the cathode in BESs. Based on the principle, anaerobic reductions of refractory substances using BESs have been studied extensively, which include nitrobenzene [19–21], copper (II) [22,23], chloroethenes [24,25], 2-chlorophenol [26], iodinated X-ray contrast media [27], and azo dyes [28,29]. Previous reports demonstrated that Alizarin Yellow R (AYR) was reduced in a two-chamber bio-cathode biocatalyzed electrolysis reactor, which was inoculated with the enriched inoculum [30]. Congo red and active brilliant red X-3B were decolorized in air-cathode single-chamber BESs, which have proton exchange membrane or microfiltration membrane as separator between electrodes [31,32]. Abiotic decolorization of acid orange 7 on the cathode was studied in a dual-chamber BES, where acetate was used as electron donor for exoelectrogens at the anode [19]. An efficient decolorization of the real dye wastewater and power generation was successfully achieved using a BES with granular carbon bioanode and biocathode [33]. However, architectures and configurations of previous dual-chamber BESs would not be ideal for full-scale applications, due to large footprint and expensive capital costs. For instance, the presence of membrane in dual-chamber BESs not only develops a pH gradient between two chambers, but also increases energy losses [34]. Thus, BESs produce low voltage in fuel cell mode or require high energy input in electrolysis mode [35]; such energy losses would be substantial in BESs fed with wastewater [36]. BES design should be optimized for wastewater treatment considering scale effects (capital costs and footprint).

An up-flow biocatalyzed electrolysis reactor (UBER) lacking membrane proposed by Wang et al. [20] is scalable. Its investments are relatively cheap due to the lack of membrane and low-cost electrode materials (graphite granular and carbon brush without metal catalysts). Moreover, the flexible position and size of anode and cathode not only makes UBER flexible for treating diverse wastewaters, but also allow UBERs to be installed easily. Using UBER configuration nitrobenzene [20] and azo dye (AYR) [28] were efficiently reduced. Previous works have shown the accumulation of intermediates during anaerobic reduction of azo dye, such as p-phenylenediamine (PPD) and 5-aminosalicylic acid (5-ASA), which would be potentially toxic [32]. Thus, we employed the aerobic bio-contact oxidation reactor (ABOR) as post-treatment to the UBER in our study in order to further oxidize the intermediates into carbon dioxide. However, existing works do not provide information on design and operation parameters essential for scale-up of UBERs (e.g. characterization of resistances in UBERs, cathode size effect, HRT effect on fates of azo dyes in UBERs, and HRT effect on reductive by-products of azo dye in post-aerobic system). In our previous study, it was found that stacked granular graphite cathode and HRT were critical for decolorizing azo dye in an UBER [29]. It confirmed that reductive by-products of azo groups (aromatic amines) were further oxidized to carbon dioxide in a post-aerobic bioreactor. While, operating conditions were not optimized in the post-system, and more information on fates of reductive by-products would be needed for field application. Hence, in this study, we first evaluated the effect of cathode size on decolorization efficiency of AYR in UBERs. Second, HRT was optimized for AYR decolorization in UBERs having different cathode sizes. Third, we assessed HRT effects on the oxidation of remaining AYR and its reductive by-products in a post ABOR. Finally, we tracked the fates of AYR by-products in an UBER and the post-aerobic bioreactor and proposed metabolic pathways in the combined bioprocess.

2. Materials and methods

2.1. Construction of UBER–ABOR

This study evaluated transformation of AYR in a continuous bioprocess that combines an UBER (Fig. 1A and B) with an ABOR (Fig. 1C). Six laboratory scale UBERs were manufactured and used for these experiments (Fig. 1B). Briefly describing, the UBER consists of a cathode zone at the bottom and an anode zone on the top without membrane. Graphite granules in a range of 3–5 mm were stacked as cathodes and a carbon brush with a diameter of 4.5 cm was used as the anode. The total volume of the UBERs was 250 mL, and the volume of anode zone was fixed at 45 cm^{-3}; refer to the literature [28,29] for details. Three different volumes of the cathode zone were set by adjusting a height of effluent ports in the UBERs, which were 45 cm^{-3} (UBER-1), 90 cm^{-3} (UBER-2) and 135 cm^{-3} (UBER-3), respectively (the working volume of the UBER was 180 mL, 160 mL, and 140 mL in order). To improve experimental reliability, two identical UBERs for each cathodic configuration under the same operating conditions were operated. The distance between the anode and the cathode was fixed at 2 cm. The UBERs were operated with external resistance of 10 and applied voltage of 0.5 V using a DC power supply (IT6921, Itech Co., Ltd., USA). A saturated calomel electrode (SCE+247 mV vs. standard hydrogen electrode) (Shanghai Precision Scientific Instruments Co., Ltd., China) was placed between the anode and the cathode to measure half potentials; here the electrode potential was reported against SCE. Three samples ports (SPs) were installed at 1.0, 6.0, and 12.0 cm above the bottom (designated as SP1#, SP2#, and SP3#) to monitor the change of chemical compositions throughout the reactors. Effluent from the UBERs was pumped to the subsequent ABOR for further oxidizing the intermediates of AYR under aerobic conditions.

2.2. Inoculation and operational conditions

The anode-respiring bacteria (ARB) were acclimated in a microbial fuel cell using carbon brush as the anode and acetate as carbon and electron source for 3 months. The carbon brushes were then transferred to the anode zone of the UBERs. The cathode zone was not inoculated with ARB to improve abiotic reduction of AYR on the cathode; a previous study showed that biofilm formation on the cathode deteriorated AYR reduction on the cathode [29]. The ABOR was inoculated with recycle activated sludge collected from Taiping municipal wastewater treatment plant in Harbin, China.

The effect of cathode volume (i.e. cathode size) on AYR reduction was evaluated in the UBERs. Three groups of UBERs with the total cathode volume (TCV) of 45 cm^{-3}, 90 cm^{-3} and 135 cm^{-3} were operated so that the anode volume to cathode volume ratio was 1:1, 1:2, and 1:3 for UBER-1, UBER-2, and UBER-3,