Journal of Hazardous Materials 299 (2015) 158–164

Contents lists available at ScienceDirect

Journal of Hazardous Materials

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

Enhanced azo dye removal in a continuously operated up-flow anaerobic filter packed with henna plant biomass

Jingang Huang[a,b,*], Mengke Wu[a], Jianjun Chen[a], Xiuyan Liu[a], Tingting Chen[a], Yue Wen[b], Junhong Tang[a], Zhengmiao Xie[a]

[a] Institute of Environmental Science and Engineering, Hangzhou Dianzi University, Hangzhou 310018, PR China
[b] State Key Laboratory of Pollution Control and Resource Reuse, College of Environmental Science and Engineering, Tongji University, Shanghai 200092, PR China

HIGHLIGHTS

- Henna stem mixed with ceramic media in UAF enhanced the removal of AO7.
- Bio-reduction was the main AO7 removal pathway in henna-added UAF.
- Adsorption and endogenous reduction were the main removal pathways in the control.
- Henna played a multiple role in providing electron donors and redox mediator.

ARTICLE INFO

Article history:
Received 7 March 2015
Received in revised form 12 May 2015
Accepted 26 May 2015
Available online 27 May 2015

Keywords:
Henna plant biomass
Up-flow anaerobic bio-filter (UAF)
Electron donor
Redox mediator
Lawsone

ABSTRACT

Effects of henna plant biomass (stem) packed in an up-flow anaerobic bio-filter (UAF) on an azo dye (AO7) removal were investigated. AO7 removal, sulfanilic acid (SA) formation, and pseudo first-order kinetic constants for these reactions (k_{AO7} and k_{SA}) were higher in the henna-added UAF (*R*2) than in the control UAF without henna (*R*1). The maximum k_{AO7} in *R*1 and *R*2 were 0.0345 and 0.2024 cm^{-1}, respectively, on day 18; the corresponding molar ratios of SA formation to AO7 removal were 0.582 and 0.990. Adsorption and endogenous bio-reduction were the main AO7 removal pathways in *R*1, while in *R*2 bio-reduction was the dominant. Organics in henna could be released and fermented to volatile fatty acids, acting as effective electron donors for AO7 reduction, which was accelerated by soluble and/or fixed lawsone. Afterwards, the removal process weakened over time, indicating the demand of electron donation and lawsone-releasing during the long-term operation of UAF.

1. Introduction

Azo dye is a widely used chemical in industrial applications. It is harmful to the environment and to human health. Therefore, wastewater containing azo dyes requires a proper treatment before it can be discharged. A combined process incorporating anaerobic reduction and subsequent aerobic oxidation, with the former reaction being the rate-limiting step, is usually applied due to the low cost and energy consumption of this process [1].

Many anaerobic bioreactors have now been successfully applied for azo dye reduction. These bioreactors include, among others, up-flow anaerobic sludge blanket (UASB) [2], anaerobic sequencing batch reactor (ASBR) [3], anaerobic baffled reactor (ABR) [4], membrane bioreactor (MBR) [5], up-flow packed-bed reactor (UPBR) [6,7] and so on. UPBR and other media-packed reactors such as up-flow anaerobic fixed bed (UAFB) and up-flow anaerobic bio-filter (UAF) have been considered for wastewater treatment due to their stable performance [8,9]. However, the hydraulic retention time (HRT) during the anaerobic reduction of azo dyes is relative long [10], resulting in the need for large size of these bioreactors.

Anaerobic reduction of azo dyes is dependent on the availability of electron donors and redox mediators (RMs). RMs can effectively shuttle electrons from the extra donor and even endogenous sub-

* Corresponding author at: Room S104, The 6th Building, Hangzhou Dianzi University, Hangzhou 310018, PR China. Tel.: +86 571 86919158; fax: +86 571 86919158.
E-mail address: hjg@hdu.edu.cn (J. Huang).

http://dx.doi.org/10.1016/j.jhazmat.2015.05.044
0304-3894/

strate to the final acceptor of the azo bond (—N=N—) [11]. Previous research has indicated that extra electron donors such as acetate, glucose and ethanol in the influent of bioreactors can serve as energy pools for effective azo dye reduction, and that the addition of RMs such as anthraquinone-2,6-disulfonate (AQDS) can accelerate this process [12]. However, a continuous dosing of soluble RMs in wastewater treatment implies an additional operation cost. Attempts have recently made to immobilize soluble RMs on inert materials, or to use solid materials containing surface RMs, thus avoiding the need for continuous addition of soluble RMs [13,14]. Although this technology has been applied in continuously operated anaerobic bioreactors [15,16], the high implementation cost still limits its wide engineering application. To overcome these drawbacks during the anaerobic reduction of azo dyes, researchers have been seeking effective and eco-friendly electron donors and RMs.

Henna (*Lawsonia inermis*), which is a large carbon sink containing abundant lawsone [17], is widely cultured over the world. Natural plant biomass such as corncobs and cattails have been proven to act as electron donors and carbon sources for the biological removal of various oxidized pollutants including nitrate and halogen-derivatives [18,19]. Besides, lawsone is an effective RM capable of shuttling electrons from the primary donor to the final acceptor of azo dyes [20]. Therefore, henna plant biomass is an economical option for the simultaneous supply of available electrons and RMs. It has previously indicated that henna leaf powder played a multiple role in donating electron, carbon and RM in batched anaerobic systems, resulting in the enhanced reduction of an azo dye [21].

In this study, henna plant biomass was mixed into the packed ceramic media of UAF for the enhanced removal of azo dyes. The aims of this study were (1) to investigate the daily performance of UAFs with and without henna packing; (2) to analyze the kinetics of azo dye removal as influenced by media height; and (3) to reveal the related mechanisms of azo dye removal that are enhanced by henna plant biomass.

2. Materials and methods

2.1. Chemicals and materials

Orange II, also known as Acid Orange 7 (AO7), which was widely used in the industrial applications, was employed as a model azo dye in this study. Commercial henna plant biomass (stem) was purchased from Bozhou City in Anhui province, China. Henna stem was dried at 45 °C for at least 8 h, and then be cut into 5 ~ 8 mm pieces before use. Ceramic with an average diameter of 3 mm was used as the main media in the UAFs, and the stacked porosity was 36%. The inoculated sludge was originally obtained from a parent sequential batch reactor which had been operated for ~150 days and achieved stable biological AO7 removals (above 90%) with glucose as co-substrate. This obtained sludge was washed for three times with de-ionized water and then was settled for 5 h. The thickened sludge was flushed with purified nitrogen gas (N_2) and then was used as inoculums. Biomass concentration of this inoculated sludge was 10 g VSS L^{-1}, and pH was 7.12.

2.2. Reactor and media

Two identical plexiglas laboratory-scale cylindrical (35 mm diameter, 500 mm height) UAF reactors (*R*1 and *R*2) were set-up in this study. The reactors were operated in an air-conditioned room at temperature of 25 ± 1 °C. Eight sampling ports were placed at 50, 100, 150, 200, 250, 300, 350 and 450 mm from the bottom of each reactor. The sampling port at 450 mm also acted as the effluent port. *R*1 was only packed with ceramic (400 mm high) and acted as a control reactor. In *R*2, 10 g of henna stem pieces were mixed into the ceramic media to investigate the effect of henna plant biomass on azo dye removal. Before packing into the UAFs, ceramic was submerged into the inoculated sludge for a week to immobilize surficial anaerobic microorganisms. The UAFs were continuously operated with a two-channel peristaltic pump at a flow rate of 300 μL min^{-1}, resulting in an HRT of 8.8 h.

Identical influent to the two UAFs were used, and was prepared in N_2-flushed, de-ionized water. The characteristics of the feed water were described as following. AO7 concentrations in the influent were kept at 0.69 mM, and the theoretical SCOD was 474 mg L^{-1}. The pH was adjusted to 7.0 ± 0.2 using a stocked $NaHCO_3$ solution (50 g L^{-1}). NH_4Cl (80 mg L^{-1}) and KH_2PO_4 (20 mg L^{-1}) were added as nutrients, resulting in the concentrations of NH_4^+—N and total phosphorus (TP) at 21 mg L^{-1} and 4.6 mg L^{-1}, respectively. Macro and trace metals and vitamins were supplied as a previous study [21].

2.3. Experimental set-up

*R*1 and *R*2 were continuously operated for about three months, during when initial stage (days 1 ~ 20), middle stage (days 21 ~ 60) and latter stage (days 61 ~ 91) were defined. To investigate the benefit of the packed henna stem on operational performance of the UAFs, frequent analyses of effluent from *R*1 and *R*2 were conducted for pH, soluble chemical oxygen demand (SCOD), volatile fatty acids (VFAs), soluble lawsone, AO7 and its reduction product of sulfanilic acid (SA) during the entire operational period. Additionally, AO7 and SA were measured simultaneously at different sampling ports on days 1, 5, 18, 41, 55, 72 and 91, to investigate the reaction kinetics of AO7 removal and SA formation as a function of media height at different operational stages. Pseudo first-order kinetic models were employed to analyze the AO7 removal and SA formation using the following equations:

$$C_{AO7(h)} = C_0 e^{(-k_{AO7}h)} \quad (1)$$

$$C_{SA(h)} = C_{max}\ (1 - e^{(-k_{SA}h)}) \quad (2)$$

where $C_{AO7(h)}$ and $C_{SA(h)}$ were the AO7 and SA concentrations (mM) at the media height of h (cm) in the UAF; C_0 is the influent AO7 concentration (mM); C_{max} is the possible maximum SA concentration (mM); k_{AO7} and k_{SA} (cm^{-1}) are the first-order kinetic constants for AO7 removal and SA formation, respectively.

Furthermore, to evaluate the adsorption of AO7 by fresh ceramic and/or henna plant biomass, three adsorption tests (A1, A2 and A3) were carried out in 250-mL serum bottles. Ceramic and henna stem pieces were firstly dry-heat sterilized (135 °C, 4.0 h) to extinguish the biological activation, and were then transferred to A1 (2.5 g henna), A2 (80 mL ceramic) and A3 (2.5 g henna + 80 mL ceramic), respectively. Afterwards, the influent feed water (100 mL) were added to the above serum bottles. The adsorption tests were conducted in triplicate at 25 °C while shaking at 150 rpm (rotations per minute). Liquid samples withdraw at appropriate time intervals were immediately detected for AO7 and SA.

2.4. Chemical analysis

Withdrawn samples were centrifuged at 4000 × *g* for 20 min, and then be filtered through 0.45 μm membrane filters. pH was measured by a portable pH meter (SANXIN, SX751, China). For AO7 analysis, the filtered samples were first diluted with freshly prepared phosphate buffer (50 mM, pH 7.0) containing ascorbic acid (500 mg L^{-1}), and then were measured spectrophoto-metrically at the wavelength of 484 nm. Soluble chemical oxygen demand (SCOD) and VSS were determined according to *Standard Methods*.