Water Research 104 (2016) 408–417

Contents lists available at ScienceDirect

Water Research

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

Inhibitory effect and mechanism of azo dyes on anaerobic methanogenic wastewater treatment: Can redox mediator remediate the inhibition?

Ruobin Dai [a], Xiaoguang Chen [a, b, *], Ying Luo [a], Puyue Ma [a], Shengsheng Ni [a], Xinyi Xiang [a], Gang Li [a]

[a] College of Environmental Science and Engineering, Donghua University, Shanghai, 201620, China
[b] State Environmental Protection Engineering Center for Pollution Treatment and Control in Textile Industry, Shanghai, 201620, China

ARTICLE INFO

Article history:
Received 29 April 2016
Received in revised form
25 July 2016
Accepted 21 August 2016
Available online 22 August 2016

Keywords:
Azo dye
Inhibitory mechanism
Specific methanogenic activity
Redox mediator
Physical characteristic
Extracellular polymeric substance

ABSTRACT

Inhibitory effect of azo dyes on anaerobic methanogenic wastewater treatment (AMWT) has been studied mainly focusing on biological toxicity in the batch test with simulated sole co-substrate. Detailed information on inhibitory effect and mechanism of azo dyes during the long-term operation with real complex co-substrate is limited. Moreover, whether redox mediator (RM) could remediate the inhibition is still unclear in previous studies, especially under the complex scenario. In this study, the real textile wastewater with alternative concentrations of azo dyes (0–600 mg/L) were used to operate a lab-scale high-rate anaerobic methanogenic bioreactor for 127 days, and 50 μM anthraquinone-2-sulfonate (AQS) as RM was added at the last period of operation. Azo dyes with concentration of 600 mg/L could cause significant inhibition on overall (decolorizing and methanogenic) performance of AMWT. Specific methanogenic activity assays showed that acetoclastic methanogens was more susceptible to high concentration azo dyes than hydrogenotrophic methanogens. The spatial distribution of extracellular polymeric substance in the anaerobic granular sludge (AGS) showed that the high biological toxicity of azo dyes was mainly attributed to enrichment effect in tightly bound-EPS (TB-EPS). The channels of AGS was clogged by azo dyes, which was evidenced by the hard release of aromatic amines in EPSs as well as decreased porosity of AGS and scanning electron microscope images. Meanwhile, the settling ability, particle size and strength of AGS all deteriorated after azo dyes concentration exceeded 450 mg/L. The dosing of AQS could mostly remediate overall performance of the bioreactor even if the recovery of acetoclastic methanogens was slow. However, except for the porosity with a part of recovery, physical characteristics of AGS hardly recovered, and washout of sludge from the bioreactor was still happening. It suggested that additional attention should be paid to prevent sludge from washout if RM was practically used to remediate the anaerobic reactor inhibited by azo dyes.

1. Introduction

The wide application of dyes made our world more colorful, but it also brought us the undesirable visible pollution. It was recorded that the total amount of dye discharged per year had exceeded one million tons since 2007 (Singh and Arora, 2011). Fifty percent of dyes discharged was azo dye, the aromatic compounds that contain one or more azo bonds (R1-N=N-R2) (Meng et al., 2012). The direct discharge of azo dye containing wastewater has adverse effects on the transparency and aesthetic of the aquatic environment. Also, some azo dyes were proven to be stable in soil, in which microbial community structure was significantly impacted (Imran et al., 2015). More importantly, many azo dyes and their cleavage products are toxic, mutagenic and/or carcinogenic to life (Umbuzeiro et al., 2005; Tan et al., 2005). The effective treatment towards azo dye is thus critical for both environmental and ecological concerns.

Combined anaerobic-aerobic biological treatment process has been regarded as the most logical concept for the treatment of azo dyes (Van der Zee and Villaverde, 2005). In the process azo dyes were anaerobically biodegraded to aromatic amines which could be

* Corresponding author. Room 4161, 2999 Renmin North Road, Songjiang District, Shanghai, 201620, China.
E-mail address: cxg@dhu.edu.cn (X. Chen).

http://dx.doi.org/10.1016/j.watres.2016.08.046
0043-1354/

further aerobically mineralized. The step of anaerobic treatment is essential because azo dyes were recalcitrant to aerobic biotreatment (Santos et al., 2007), and for some bacterial strains azo dyes were recalcitrant under aerobic condition but easily biodegradable under anaerobic condition (Deng et al., 2008). Unfortunately, preliminary studies have demonstrated that high/medium concentration azo dyes could biologically inhibit the anaerobic methanogenic wastewater treatment (AMWT) (Sponza and Isik, 2004; Hong et al., 2007; Alvarez et al., 2015). In addition, the competition for reducing equivalents between dye reducers and methanogens would happen when azo dyes and co-substrate were existed simultaneously (Santos et al., 2006). As the negative impact of azo dyes on AMWT may lead to low efficiency and/or even breakdown for the AMWT, precise understanding of the impact was particularly crucial for us to remediate the effected AMWT. However, most of studies only included short-term exposure to azo dyes in batch tests with simulated sole co-substrate, while detailed continuous tests with respect to long-term exposure using real complex co-substrate were still limited (Van der Zee et al., 2003; Brás et al., 2005). Meanwhile, the inhibitory mechanism of azo dyes was often studied focusing on biological toxicity. After an extended period of time, the toxic or competitive effect of azo dyes may not only lead to volatile fatty acid (VFA) accumulation, decrease of methane production or low azo dye degradation efficiency, but also may clog channels in anaerobic granular sludge (AGS). Moreover, the azo dyes or their cleavage products may change the physical characteristics or impair the production of extracellular polymeric substance (EPS) of sludge (Sheng et al., 2010), which may lead to disintegration, floating, washout of the granular sludge. For these reasons, we believe that a comprehensive continuous test is important to reveal detailed information about the inhibitory effect and mechanism of azo dyes on the performance of AMWT.

Redox mediators (RMs) (such as anthraquinone-2-sulfonate (AQS)) have been evidenced to catalyze the anaerobic reduction of azo dyes (Van der Zee and Cervantes, 2009). For instance, Santos et al. (2004) found that AQS could accelerate the anaerobic bioreduction of azo dyes for up to 2.67-fold, via decreasing the activation energy for 1.2-fold. The presence of redox mediators may reduce the inhibitory effect of azo dyes on AMWT by catalyzing azo dye biodegradation. But whether RM can remediate the overall performance of the bioreactor and physical characteristics of sludge is unknown up to now.

Within diverse application fields of azo dyes, the textile industry accounted for a large fraction (Santos et al., 2007). Hence the real textile wastewater with alternative concentrations of azo dyes was employed to feed a lab-scale high-rate anaerobic methanogenic bioreactor. The overall performance of the bioreactor as well as methanogenic activity, physical characteristics and EPS of sludge were monitored to assess the inhibitory effect and mechanism of azo dyes on AMWT. The AQS (i.e. RM) was added at the last period of operation to evaluate whether RM could remediate the inhibition.

2. Materials and methods

2.1. Wastewater

The textile dyeing wastewater from the cotton textile industry generally consists of the pre-treatment wastewater (i.e. mixture of wastewaters from desizing, scouring/washing, bleaching and mercerizing processes) and the dyeing wastewater (i.e. mixture of wastewaters from dyeing, rinsing and finishing) (Santos et al., 2007). The wastewater used in this study was the mixture of real pre-treatment wastewater and synthetic dyeing wastewater, with a proportion of 1:1.

2.1.1. Pre-treatment wastewater

Real pre-treatment wastewater was collected from a regulating tank, in which pH of the wastewater was adjusted to 7.0–7.6 by hydrochloric acid, in a cotton textile dyeing wastewater treatment plant at Yixing, Jiangsu Province, China. In the pre-treatment process, the sizing agents discharged were polyvinyl alcohol (PVA, approx. 30%–40%), carboxymethylcellulose (CMC, approx. 10%–20%) and starch (approx. 50%). Auxiliaries used mainly included hydrogen peroxide, disinfectants, surfactants, brighteners, etc. The characteristics of the wastewater were listed in Table 1. The real pre-treatment wastewater was stored at 4 °C before use.

2.1.2. Synthetic dyeing wastewater

Synthetic dyeing wastewater consisted of nutrients (2 mL/L), NaCl (10 g/L) as well as azo dyes, which were diluted from a stock dye solution (50 g/L) that was adjusted by NaOH to pH 12 and then hydrolyzed at 80 °C for 1.5 h (O'Neill et al., 2000a). The adding amount of the stock dye solution depended upon the experimental conditions. Acid orange 7 (AO7, $\lambda_{max} = 484$ nm), reactive red 2 (RR2, $\lambda_{max} = 539$ nm), reactive black 5 (RB5, $\lambda_{max} = 595$ nm), direct yellow 12 (DY12, $\lambda_{max} = 405$ nm) and direct blue 71 (DB71, $\lambda_{max} = 579$ nm) were equally contained in the stock dye solution, and structure formulas of azo dyes used in this study was given in Fig. S1. These azo dyes were bought from Shanghai Jiaying Chemical Engineering Co., Ltd., China. The strength of dyes were 100% except for DY12 (80%). The nutrients included trace element solution I, II and nutrition solution of 1 mL/L, which were prepared according to Tang et al. (2013).

2.2. Experimental set-up, inoculation and reactor operation

A spiral symmetry stream anaerobic bioreactor (SSSAB) with working volume of 18.7 L was used to treat the wastewater. The configured parameters and schematic of the SSSAB were previously detailed (Chen et al., 2016). In the reaction zone (middle part of the reactor) of SSSAB three elliptic plates were set 120° spirally and symmetrically. The sludge bed was then divided into three chambers by the elliptic plates. The reaction zone were provided with an insulation layer for keeping the temperature as 35 ± 1 °C in the reaction zone. Peristaltic pumps were used for pumping the influent and circulating hot water.

The bioreactor was seeded with 9.2 L sludge. The seed sludge was inoculated with methanogenic granular sludge from the bottom of a full-scale internal circulation reactor treating wastewater in a papermaking plant at Wuxi, Jiangsu Province, China. The mean diameter of the seed sludge was 2.2495 mm, and its density and VSS/SS were 1.17 g/cm^3 and 0.77, respectively.

The hydraulic retention time of the bioreactor was 30 h throughout the experiment. Three periods of operation can be distinguished. As shown in Table 2, after inoculation, the reactor

Table 1
Characteristics of real pre-treatment wastewater.

	pH	COD (mg/L)	NH_4^+-N (mg/L)	Total phosphorus (mg/L)	Suspended solids (SS, mg/L)	SO_4^{2-} (mg/L)	Conductivity (mS/cm)
Real pre-treatment wastewater	7.5 ± 0.1	4160 ± 150	80.2 ± 10.1	18.3 ± 3.5	430.5 ± 103.7	42.1 ± 6.2	9.56 ± 0.80