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Mixed dye wastewater treatment in a bioelectrochemical system-centered process

Min-Hua Cui[a,b], Lei Gao[b], Hyung-Sool Lee[c], Ai-Jie Wang[b,d,*]

[a] Jiangsu Key Laboratory of Anaerobic Biotechnology, School of Environmental and Civil Engineering, Jiangnan University, Wuxi 214122, PR China
[b] State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, 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 Environmental Biotechnology, Research Center for Eco- Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, PR China

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ABSTRACT

The feasibility of mixed dye wastewater treatment was evaluated with a novel integrated bioprocess that consisted of a hybrid anaerobic reactor (HAR) with a built-in bioelectrochemical system, an aerobic biofilm reactor (ABFR) and a denitrification reactor (DR). The position of the DR significantly affected chemical oxygen demand (COD) and colority in effluent, and placing the DR after the ABFR improved effluent quality probably due to minimization of the undesired autoxidation of aromatic amine in dye wastewater. The optimal integrated process of HAR + ABFR + DR efficiently treated mixed dye wastewater, and concentrations of COD and TN were decreased down to 75 ± 18 mg/L and 12.91 ± 0.31 mg/L, respectively, along with colority 48 ± 4 times. Total phosphorus reduced to below 0.5 mg/L with coagulation using poly aluminum chloride, and the effluent quality fully met the discharge standard. This comprehensive study suggests the feasibility of the BES based process for practical application to mixed dye wastewater treatment.

1. Introduction

There are approximately 2500 national and provincial development and industrial zones have been established across China in these days (Chinese national development and reform commission, 2018). This industrial centralization including the textile, dyeing and printing industry accounts for around 60% of gross domestic products, but also high-polluting sources in China (Geng and Doberstein, 2008). To better protect water body from contaminants in these zones, industries are compulsory to pretreat wastewater on-site, and then pre-treated wastewater is transported to centralized wastewater treatment plants. Most of the centralized wastewater treatment facilities also receive domestic wastewater, together with industrial wastewater (called, mixed dye wastewater) as shown in Table 1. The characteristics of the mixed dye wastewater are varied with the mixing ratio and composition of the influent. However, the mixed wastewater commonly manifested low to moderate organic strength, low biodegradability, intensive colority, relatively high nutrients (Hu et al., 2013). Due to the characteristics of the mixed wastewater the centralized wastewater treatment plants have struggled to meet the increasing wastewater discharging standard: chemical oxygen demand (COD) 80 mg/L, total nitrogen (TN) 15 mg/L, total phosphorus (TP) 0.5 mg/L, and colority 50 times.

The major pollutants in the mixed dye wastewater are the residual dyestuffs and additives. Although the advanced oxidation processes such as Fenton, electrocatalysis, ozone, and electrochemical oxidation have presented excellent performance by mineralizing the contaminants (Boudissa et al., 2019; Park et al., 2018; Shi et al., 2018; Zhu et al., 2011), the high cost and extreme operating conditions (e.g., extreme pH, high conductivity and violent reaction courses) seem to be the technical and operational barrier for large-scale application. Alternatively, cost-effective biological treatment has been widely used for dye wastewater. The anaerobic reduction is the indispensable step for biological treatment of the mixed dye wastewater because most dyestuffs are stable under aerobic condition. Typical anaerobic processes, however, suffered from low treatment efficiency (Cui et al., 2017a). Interestingly, literature has reported that bioelectrochemical system (BES)-based anaerobic processes can improve treatment of recalcitrant dyes wastewater (Cui et al., 2014a; Cui et al., 2018; Cui et al., 2019a). With small applied voltage (normally less than 1 V), removal efficiency of dyes can be significantly enhanced (Cui et al., 2019b). For instance, Cui et al. installed BES modules into a four-compartment anaerobic baffled reactor to enhance reduction of the azo dye Alizarin Yellow R and showed that decolorization efficiency reached 95.1 ± 1.5% at hydraulic retention time (HRT) of 5 h and applied a voltage of 0.5 V

* Corresponding author at: State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin 150090, PR China.
E-mail address: waj0578@hit.edu.cn (A.-J. Wang).

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Table 1
Summary of typical mixed dye wastewater treatment plants in China.

Location	Treatment capacity ($\times 10^4$ t/d)	Composition of influent (percentage)
Fengxin industrial park, Yichun, Jiangxi	2.5	Printing and dyeing wastewater (60%), domestic wastewater (40%)
Changshu, Jiangsu	2	Printing and dyeing wastewater (80%), domestic wastewater (20%)
Textile printing and dyeing circular economy industrial park, Jingzhou, Hubei	8	Printing and dyeing wastewater (85%), domestic wastewater (15%)
Xiaoshan, Hangzhou, Zhejiang	100	Dye manufacture, printing and dyeing, chemical wastewater (90%), and domestic wastewater (10%)
Binhai industrial zone, Shaoxing, Zhejiang	90	Dye manufacture, printing and dyeing, chemical wastewater (90%), and domestic wastewater (10%)
Huzhou, Zhejiang	3	Dye manufacture (80%), printing and dyeing (10%), other industrial wastewater (10%), domestic wastewater (10%)
Bleaching, printing, and dyeing production base, Ningbo, Zhejiang	5	Influent mainly comes from dye manufacture, printing and dyeing industries

(Cui et al., 2014b). BES-based hybrid processes proved to increase dye removal rate over control (solely anaerobic bioreactor without BES), while synthetic dye wastewater was only used in literature (Cui et al., 2017a). To accelerate deployment of BES-based hybrid processes for dye wastewater treatment, more studies using real wastewater would be essential.

In addition to dye removal, we also need to control COD and nutrients because of the wastewater discharge standard (Chen et al., 2011), as discussed above. To meet the standard, post-treatment to BES-based hybrid processes is required. However, information on biological post-treatment technologies is minimum. Typical biological nitrogen removal processes (e.g., nitrification and denitrification) could be added to the BES hybrid processes for nitrogen control, but the unique characteristics of the mixed dye wastewater can lead to uncertainty and instability on COD and colority removal in post-treatment, such as the autoxidation of aromatic amines (Katheresan et al., 2018). Aromatic amines are pervasive products from the anaerobic reduction of dyes, which can be removed in the subsequent anoxic/aerobic process mainly through biodegradation and autoxidation. Complete biodegradation of aromatic amines is an ultimate pathway to simultaneous removals of organic matter and colority. However, autoxidation of aromatic amines will potentially produce stable, water-soluble, highly colored compounds, resulting in a high COD and intensive colority in effluent (van der Zee and Villaverde, 2005). The oxygen level is a critical parameter affecting biodegradation and autoxidation rates of aromatic amines (Wang et al., 2012), and hence, it is very important to design and optimize post-treatment bioprocesses for simultaneously removing COD, colority, and nitrogen.

In this study, an integrated process that consists of a hybrid anaerobic-bioelectrochemical reactor (HAR), an aerobic biofilm reactor (ABFR) and a denitrification reactor (DR) was designed and tested for mixed dye wastewater treatment. Using model azo dye acid orange 7 (AO7) contained domestic wastewater we first evaluated the performance of individual bioreactors on removals of COD, colority, and nitrogen including nitrification efficiency in two integrated processes: HAR + ABFR + DR and HAR + DR + ABFR. Based on effluent quality we selected a superior treatment process, focusing on effluent colority. Treatment of mixed dye wastewater was then comprehensively evaluated in the selected process, and we finally assessed coagulation using poly aluminum chloride for TP control, as well as other water quality parameters. This study proves the applicability of the BES-based biological treatment process for mixed dye wastewater treatment.

2. Material and methods

2.1. Configuration of bioreactors

An integrated process consisted of three units, as shown in Fig. 1: a hybrid anaerobic reactor (HAR), an aerobic biofilm reactor (ABFR) and a denitrification reactor (DR). Three reactors fabricated with plexiglass have an empty volume of 1.25 L approximately with the inner diameter of 8 cm and a height of 25 cm. One pair of electrodes was installed in the upside of the reactor. Granular graphite (diameter from 3 to 6 mm, Linzhang county Deyuan carbon co., LTD, Handan, China) was used for both the anode and the cathode (8 cm in diameter and 4 cm in height). The distance between the anode and the cathode was 2.5 cm, and the total volume of the electrodes was 400 cm^3 in the HAR. Before use, the granular graphite was pretreated by soaking it in 32% HCl solution for 24 h to remove inert materials (Mu et al., 2009). Graphite rod (Φ = 4 mm) equipped at the electrode zone in the HAR was used as a current collector. A saturated calomel electrode (SCE, +247 mV vs. standard hydrogen electrode, model-217, Shanghai Precise Sci. Instru. Co., Ltd. China) was used as the reference electrode in the HAR, and we monitored electrode potential against the reference electrode during the experiments. A constant voltage of 0.5 V was supplied between the anode and the cathode with a DC power supply (FDPS-180, Fudan Tianxin Scientific and Educational Instruments Co., Ltd, Shanghai, China). A 10 Ω resistor was equipped in external wires to monitor electrode potential and voltage in the HAR. The voltage across this resistor was recorded every 10 min with a data acquisition system (Keithley 2700, Keithley Co. Ltd., U.S.), which were automatically converted to current according to Ohm law.

Approximately 800 mL of granular graphite was filled in the ABFR and served as the fillers for supporting biofilm growth. The property and pretreatment procedure of granular graphite fillers were identical with those used for the HAR. An aerator with a diameter of 5 cm was installed into the reactor for supplying oxygen gas. An air pump (ACO-9610, Hailea, Hailea Group Co., Ltd, China) was connected to the aerator and a gas flowmeter was used to control the aeration rate. The DR was identical to the ABFR without the aerator.

2.2. Inoculation of bioreactors and operating conditions

The BES of HAR was inoculated with domestic wastewater sampled from a local manhole of sewage pipeline was amended with sodium acetate (NaAc, 1000 mg/L) and azo dye AO7 (200 mg/L), and we fed the HAR with this amended wastewater in batch mode. Table 2 summarizes the characteristics of domestic wastewater. When current-time profiles were replicated in batch operation, 400 mL anaerobic sludge, that had been sampled from an up-flow anaerobic sludge blanket treating azo dye wastewater for more than six months (Cui et al., 2016c), was added into the bottom of the HAR to stimulate bioreduction of azo bond, along with bioelectrochemical reduction. Literature suggested that exoelectrogens oxidized biodegradable organic matters, transferred electrons to anodes, and circuited electrons could be used for cathodic reduction of azo dye. This hybrid reduction can improve reduction rate of azo dye, as compared to sole anaerobic bioreduction of the azo bond (Cui et al., 2016b). After batch operation in two more

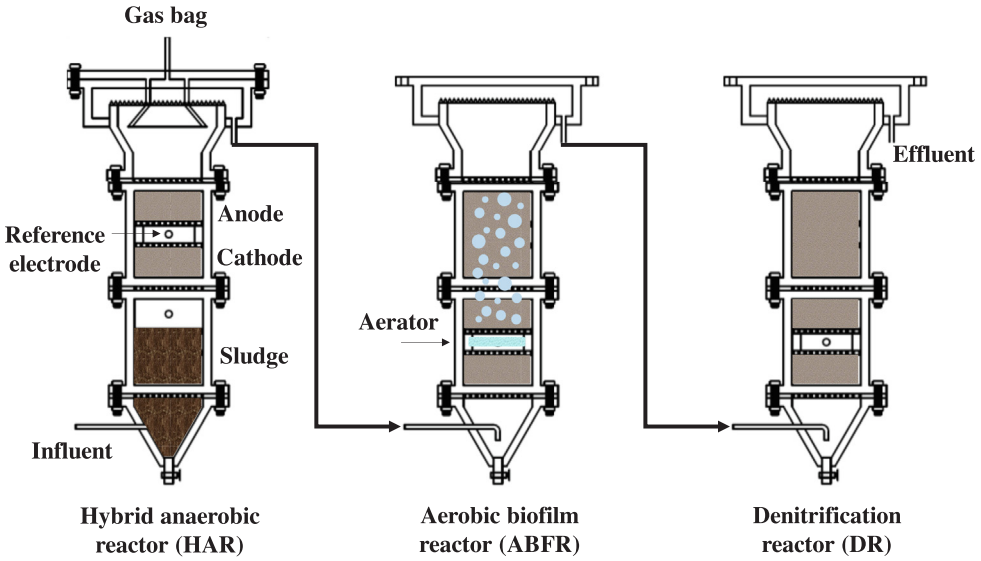

Fig. 1. Schematic of the integrated bioprocess.

Table 2
The characteristics of domestic wastewater used in the experiments.

Item	Value	Unit
COD	236 ± 23	mg/L
Colority	6 ± 2	times
TN	61.36 ± 4.70	mg/L
NH_4^+-N	55.58 ± 3.20	mg/L
NO_3^--N	0.28 ± 0.08	mg/L
NO_2^--N	0.23 ± 0.19	mg/L
TP	6.35 ± 0.39	mg/L
pH	7.19 ± 0.16	–

weeks, the HAR was switched to continuous mode by feeding wastewater with a peristaltic pump (BT100-1 L/YZ1515, Longer Pump Co., Ltd., China).

Both ABFR and DR were inoculated with the domestic wastewater sampled from the local manhole. We supplemented the wastewater with electron donors to enrich heterotrophic aerobes and heterotrophic denitrifiers, respectively, for the ABFR and the DR. We added 1000 mg/L of glucose to the domestic wastewater and operated the ABFR in batch mode during acclimation. To acclimate the DR, we ran the DR in batch mode with the domestic wastewater amended with 1000 mg/L NaAc and 100 mg/L nitrate. After COD removal and denitrification efficiency reached steady state we switched operation of the two bioreactors to continuous mode by feeding HAR effluent to the sequential ABFR and DR (see Fig. 1) with a peristaltic pump (BT100-1 L/YZ1515, Longer Pump Co., Ltd., China). The dissolved oxygen (DO) concentration in the ABFR was kept at 2–4 mg/L by controlling the gas flowmeter during the experiments.

The combined bioprocess was operated at three stages, as shown in Table 3. In stage I, the domestic wastewater amended with 200 mg/L AO7 was fed to the HAR-ABFR-DR process continuously. To determine the appropriate position of the DR in the combined process, we evaluated two different sequences: (1) HAR + ABFR + DR and (2) HAR + DR + ABFR. For the latter, the effluent from the ABFR was 100% recycled back to the DR for denitrification (1Q recycle against influent flow rate Q). In stage II (HAR + ABFR + DR) we added acetate (sodium acetate) to the DR as the exogenous electron donor. Acetate dosage was gradually increased from 90 to 120 mg-COD/L, which corresponds to 1–1.35 of the theoretical COD requirement for denitrification. In stage III, we assessed the optimized process of HAR + ABFR + DR with dye wastewater. To mimic real dye wastewater we added 8 types of dyes (from three typical categories, azo dye, anthraquinone dye, and triarylmethane dye) and three types of commonly-used additives to domestic wastewater. We gradually increased the concentration of mixed dyes from 50 to 200 mg/L. Table 4 provides detailed information on the dyes and additives used for wastewater preparation.

The open circuit control experiment was conducted at influent dye concentration of 200 mg/L to identify the contribution of BES in the integrated process (HAR + ABFR + DR). In order to fully satisfy the effluent standard, we removed TP using poly aluminum chloride (PAC, Al_2O_3 content > 28%, Guangfu fine chemical, Tianjin, China). PAC solution 5% (w/w) was prepared, and PAC dosage was optimized for coagulation. The coagulation experiments were conducted with a 500 mL Erlenmeyer flask which was equipped with a magnetic rotor and placed on a magnetic stirrer (84–1, Shanghai Meiyingpu Instruments Co., Ltd., China) for rapid mixing (200 rpm) in 2 min and flocculation (50 rpm) in 13 min followed by sedimentation for 15 min.

All of the experiments were carried out at ambient temperature (23 ± 2 °C). Effective HRTs for the HAR, ABFR, and DR were set at 3.8 h, respectively, a totally 11.4 h in the integrated process. For each condition, the reactors were run for at least 10 days (21 HRTs) to reach steady state. Chemical analyses were carried out in quintuplicate, and

Table 3
Operating conditions and influent characteristics for the experiments.

Stage	Combined processes	Acetate dosage to DR	Dye concentration/Colority	Influent
I, Optimization of combined processes	HAR + ABFR + DR, HAR + DR + ABFR	–	200 mg-AO7/L	DW + AO7
II, Optimization of carbon dose to DR	HAR + ABFR + DR	90, 100, 110, 120 mg-COD/L	200 mg-AO7/L	DW + AO7
III, Feasibility in treating complex dye wastewater	HAR + ABFR + DR	160 mg-COD/L	373 ± 46 to 1400 ± 161 times	DW + mixed dyes + Additives

HAR: Hybrid anaerobic reactor; ABFR: Aerobic biofilm reactor; DR: Denitrification reactor; DW: Domestic wastewater; AO7: Acid orange 7.

Table 4
The classification and composition of dyes and additives.

Category	Common name	CAS number	Molecular formula	Concentration (mg/L)
Azo dye	Acid Orange 7	633-96-5	$C_{16}H_{11}O_4N_2SNa$	30
	Alizarin Yellow R	2243-76-7	$C_{13}H_9O_5N_3$	30
	Congo Red	573-58-0	$C_{32}H_{22}O_6N_6S_2Na_2$	30
	Ponceau S	6226-79-5	$C_{22}H_{12}O_{13}N_4S_4Na_4$	30
Anthraquinone dye	Alizarin Red	130-22-3	$C_{14}H_7O_7SNa$	30
	Acid Green 25	4403-90-1	$C_{28}H_{20}O_8N_2S_2Na_2$	30
Triarylmethane dye	Fuchsin Basic	58969-01-0	$C_{20}H_{20}N_3Cl$	10
	Acid Fuchsin	3244-88-0	$C_{20}H_{17}O_9N_3S_3Na_2$	10
Additives	Sodium Chloride	7647-14-5	NaCl	200
	Sodium Carbonate	497-19-8	Na_2CO_3	200
	Sodium Sulfate	7757-82-6	Na_2SO_4	200

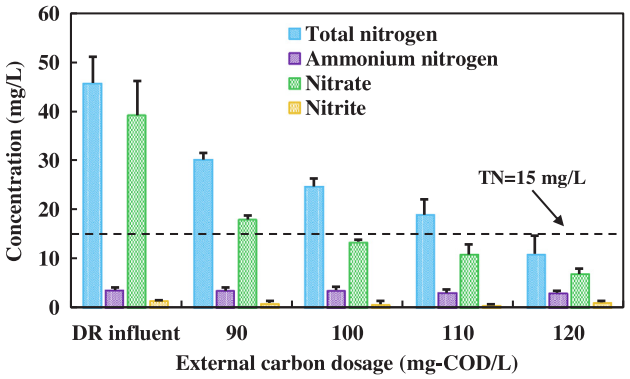

Fig. 2. The concentration of nitrogen species in the DR (denitrification reactor) effluent to acetate dose. Acetate was used for the exogenous carbon source to denitrification.

average data were reported with standard deviations.

2.3. Analytical methods

All samples were filtered with syringe filters (pore size: 0.45 μm, Tianjin Jinteng Experiment Equipment Co., Ltd., China) before analysis. The concentrations of COD, colority, ammonium nitrogen, nitrate, nitrite, TN and TP were quantified with the Standard Methods (China EPA, 2002). AO7 concentration in samples was quantified with an UV/Vis spectrophotometer (UV-1800, Shanghai Meipuda instrument Co., Ltd., China) at a wavelength of 484 nm.

3. Results and discussion

3.1. Assessment of integrated process performance

3.1.1. Significance of the position of denitrification reactor for effluent quality

Biodegradation of aromatic amines (azo dye) is an ultimate pathway to completely remove organic matter and colority. We should mitigate the autoxidation of aromatic amines in aerobic conditions because of high COD and intensive colority created by autoxidation (van der Zee and Villaverde, 2005). To simultaneously achieve AO7 decolorization and removal of aromatic amine, we evaluated the contribution of the DR in two different integrated processes of HAR + ABFR + DR and HAR + DR + ABFR.

The HAR demonstrated a high decolorization efficiency of 95.7% in 6 h. This result is consistent with previous studies showing stable decolorization of AO7 in hybrid anaerobic reactors (Cui et al., 2016e). In the HAR + ABFR + DR process, most of AO7 was further removed in subsequent treatment steps and no obvious adsorption was found at the wavelength > 380 nm in the final effluent. In comparison, the final effluent from the HAR + DR + ABFR process presented absorbance at a wide range of wavelengths and even more intensive color than the HAR effluent. This result is consistent with dark brown effluent from the HAR + DR + ABFR. It seems that autoxidation of aromatic amines in the aerobic bioreactor (ABFR) may increase colority in the final effluent from HAR + DR + ABFR. Most of aromatic amines produced from dye decolorization are stable under anaerobic conditions but prone to autoxidation in low oxygen conditions (Jonstrup et al., 2011). The autoxidative products often have colors and they are also recalcitrant and toxic polymers (Menezes et al., 2019; Thung et al., 2018). Hence autoxidation of aromatic amines can deteriorate removals of both color and COD in dye wastewater treatment (Pereira et al., 2015). We identified that COD concentration in the final effluent was 52 ± 9 mg/L in the HAR + ABFR + DR but increased to 98 ± 22 mg/L in the HAR + DR + ABFR. We thus focused on the HAR + ABFR + DR process due to high decolorization and COD removal.

3.1.2. Optimization of acetate dose for denitrification in DR

The HAR + ABFR + DR process can meet the requirements of decolorization and COD removal, but nitrogen control can be limited in this process due to lack of electron donors for denitrification in the DR; most of the biodegradable matters can be oxidized in the ABFR (aerobic conditions) prior to the DR. To achieve the goal of effluent TN concentration < 15 mg/L, the discharge nitrogen standard of water pollution for dyeing and finishing of the textile industry, we optimized acetate dose in the DR. Fig. 2 shows the concentrations of main nitrogen species and TN in the DR influent and effluent. TN concentration was averaged at 45.74 ± 5.39 mg/L in the DR influent (ABFR effluent), and nitrate was the dominant nitrogen species with small ammonium and nitrite concentration. Nitrate concentration was gradually decreased with increasing acetate dose, and the effluent TN concentration became low at 10.86 ± 3.68 mg/L at an acetate dosage of 120 mg-COD/L, meeting the discharge nitrogen standard. In this condition, the electron donor to nitrate ratio was 3.7 mg-COD/mg-nitrate, which was 32% higher than the theoretical value of 2.8 mg-COD/mg-nitrate.

3.2. Performance of the integrated process for treatment of mixed dye wastewater

3.2.1. Decolorization and COD removal of the integrated process

To reflect the complex characteristics of actual printing and dyeing wastewater, such as multi-component, high salts concentration and alkaline pH (Chen et al., 2011), eight kinds of dyes (belong to 3 categories) and three salts were mixed to mimic dye wastewater for experiments. The influent colority was increased from 373 ± 46 to 1400 ± 173 times at the increase of mixed dye concentration from 50 to 200 mg/L, as shown in Fig. 3A. The HAR mainly decolorized the dye wastewater in the integrated process (HAR + ABFR + DR), as we expected. More than half to the influent colority was removed by anaerobic sludge in all initial mixed dye concentration levels followed by the BES accounting for decolorization efficiency in a range of 29.20 ± 0.30–34.50 ± 1.50% (Fig. 3B). The colority in the final

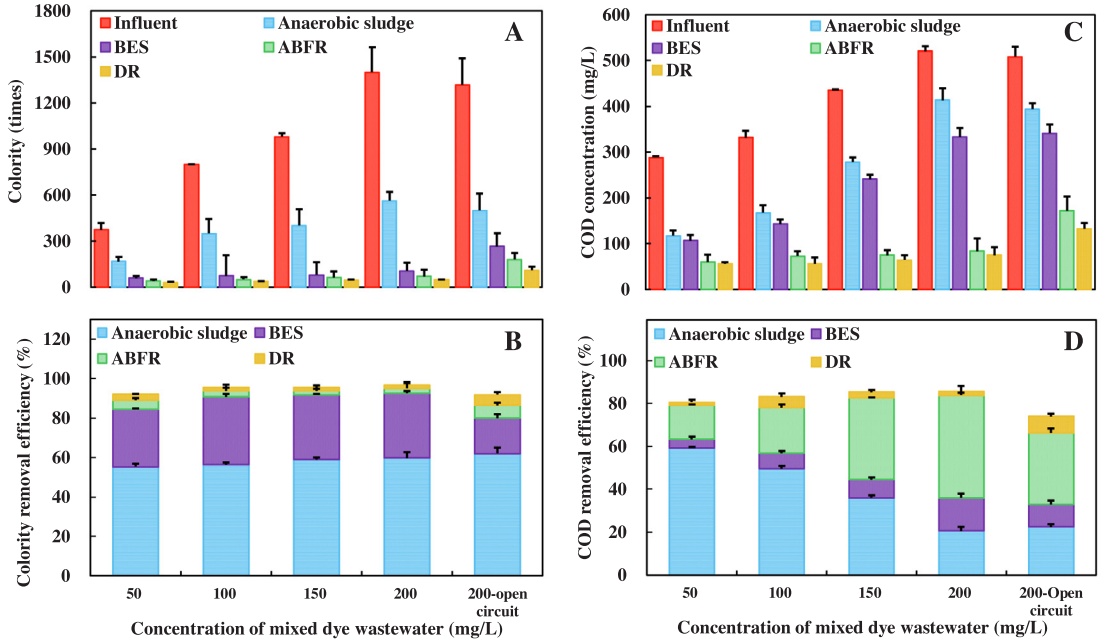

Fig. 3. Effluent colority (A), colority removal efficiencies (B), COD (C) and COD removal efficiency (D) of different units at varying mixed dyes concentration.

effluent was 48 ± 4 times at influent mixed dye concentration of 200 mg/L, meeting the discharge colority standard for dyeing and finishing of the textile industry. To precisely assess the contribution of bioelectrochemical reactions on the decolorization process, the HAR was run under open circuit mode at the influent mixed dye concentration of 200 mg/L. Colority removal efficiency of the electrodes module decreased down to 17.84 ± 2.20% and the final effluent colority increased to 109 ± 23 times. This result emphasized the importance of the contribution of bioelectrochemical reactions to dye decolorization in the combined process.

The influent COD was increased from 288 ± 3 to 520 ± 11 mg/L with increasing the mixed dye concentration. Contrary to high decolorization efficiency in the HAR, COD removal efficiency in the HAR decreased with increasing dye concentration probably because decolorization intermediates (such as aromatic amines) under anaerobic conditions might be accumulated (Cui et al., 2016d). In comparison, the ABFR efficiently removed COD and effluent COD concentration ranged from 60 ± 16 mg/L to 84 ± 27 mg/L (corresponding to COD removal efficiencies of 16.0 ± 0.3% to 47.9 ± 1.1%), as shown in Fig. 3C and D. This result supports that decolorization intermediates are well oxidized in aerobic conditions (van der Zee and Villaverde, 2005). Pan et al. (2018) reported that the aromatic amines from azo dye could be efficiently removed with bioelectrochemical reduction followed by an aerobic membrane biofilm reactor. The COD concentration before and after the DR was not changed, indicating that acetate dose 120 mg COD/L would be almost utilized for denitrification. The open circuit mode in the bioelectrochemical system did not change COD concentration much for the HAR, but COD removal in the downstream process (ABFR and DR) was affected (Fig. 3C and D). This result implies that dye compounds would not be susceptible to aerobic degradation in the ABFR. This interpretation is consistent with high colority in effluents from the HAR (open circuit) and ABFR. Consequently, the final COD concentration was increased to 132 ± 13 mg/L in the combined process under open circuit mode.

Electrode potentials in the BES were stable with influent mixed dye concentration increased from 50 to 200 mg/L, as shown in Fig. 4. The cathode potentials were varied in the range of −766 ± 29 to −806 ± 17 mV, which was in a range of cathode potential observed for efficient dye removal in literature (Cao et al., 2019; Cui et al., 2016a; Cui et al., 2017b; Yang et al., 2019). Stable anode potential

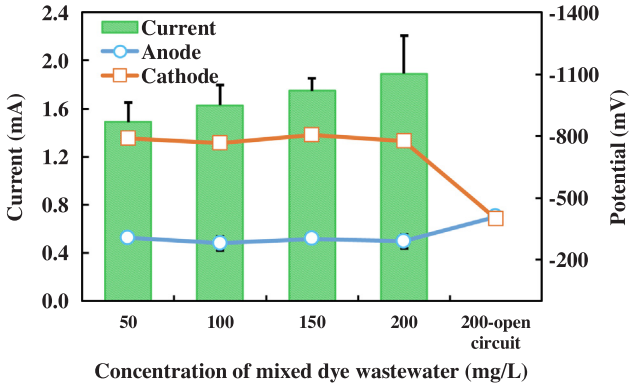

Fig. 4. Potentials and currents of BES at varying mixed dyes concentration.

implies that the high concentration (200 mg/L) dyes and additives would not influence exoelectrogens metabolism and anodic current. The current was slightly increased from 1.49 ± 0.17 mA to 1.89 ± 0.31 mA with increasing dye concentration, while decolorization efficiency was kept steady at 29.20 ± 0.30%–34.50 ± 1.50%. Higher conductivity in increased dye concentrations might improve current slightly (Kong et al., 2015).

3.2.2. Nutrients removal of the integrated process

Fig. 5 shows the effluent concentrations of nitrogen species (TN, ammonium nitrogen, nitrate, and nitrite) in each unit of the integrated process (HAR + ABFR + DR). The influent TN concentration was slightly increased with increasing mixed dyes due to nitrogen content in the dyes. High nitrification efficiency was obtained in the ABFR and nitrate concentration was 35.28 ± 0.70–50.69 ± 0.16 mg/L in the ABFR effluent; nitrite concentration was consistently small at 2.96 ± 1.46–3.82 ± 0.80 mg/L during the experiments (Fig. 5C). The DR achieved denitrification efficiency of 78.1%–86.3% at acetate dose ~160 mg/L (approximate to 1.32 times of theoretical requirement), and nitrate concentration decreased at 6.95 ± 4.60–8.28 ± 0.06 mg/L. As a result, TN concentration in the final effluent became 10.62 ± 1.40–13.08 ± 1.51 mg/L, meeting the discharge nitrogen standard for dyeing and finishing of the textile industry.

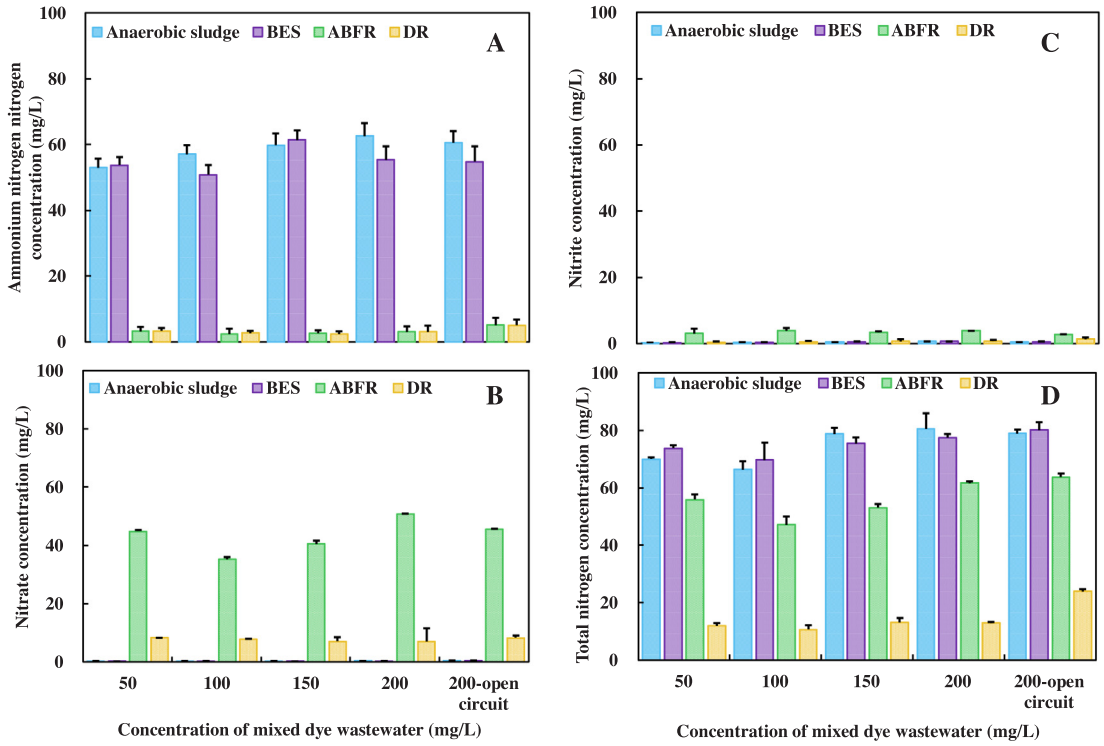

Fig. 5. Nitrogen transformation and removal at varying mixed dyes concentration (A, Ammonium nitrogen; B, Nitrate; C, Nitrate; D, Total nitrogen).

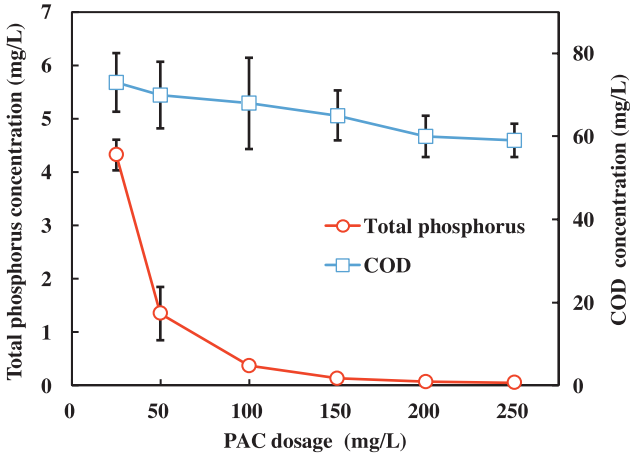

Fig. 6. Effect of PAC dosage on total phosphorus and COD removal.

The integrated process fully meets the discharge standard (colority, COD and TN) for dyeing and finishing of the textile industry, except for TP (≤0.5 mg/L). Hence, we evaluated the effectiveness of TP control with coagulation using PAC. TP concentration in the final effluent from the integrated process was stable at 5.92 ± 0.52 mg/L (influent 6.35 ± 0.39 mg/L). Fig. 6 shows the reduction of TP concentration to PAC dose. TP concentration was as low as 0.37 ± 0.05 mg/L (94.2 ± 0.8%) at PAC dosage 100 mg/L, meeting the TP standard of less than 0.5 mg/L. COD concentration was also slightly reduced from 73 ± 7 mg/L to 68 ± 11 mg/L in the coagulation.

3.3. Implication

The BES technology has been employed to deal with multiple contaminants, e. g. halogenated compound (Chen et al., 2018; Liang et al., 2019; Lin et al., 2019), nitro-compounds (Shen et al., 2014), sulfate (Blazquez et al., 2016) and dyes (Cui et al., 2020). Most of those dyes are azo dyes since the bioelectrochemical decolorization mechanism was clearly revealed as azo bond cleavage (Mu et al., 2009). However, in the practical scene, the printing and dyeing wastewater generally contained various dyes (not only azo dyes) as well as multitudinous additives. To our best knowledge, the current work was the first successful trial to use a BES-centered integrated process to treat mixed dye wastewater that containing diversified dyes, additives, and real domestic wastewater, and provide an alternative involving BES technology to industrial-scale application.

In this work, the total effective HRT of the optimal integrated process of HAR + ABFR + DR was 11.4 h, which was obviously shorter than the traditional combined process that used to remedy mixed printing and dyeing wastewater. Hu et al., assembled a process that consisted of a hybrid anaerobic baffled reactor and a cross-flow aerobic sludge reactor to treat mixed printing and dyeing wastewater, the final effluent COD was below 100 mg/L while the HRT were 12 and 20 h for two reactors (Hu et al., 2013). To short the treatment HRT was favorable to capacity expansion of the wastewater treatment plants in the context of stricter environmental protection policy in China.

Considering the significant enhancement of the BES assisting the anaerobic unit, the operational cost ascension duo to the power consumption was acceptable. In our work, the external supplied for dye treatment in the HAR was 0.5 V and the current varied from 1.5~1.9 mA. Besides, the domestic wastewater could serve as the electron donor to drive the dye reduction in the HAR, the fee for external carbon source could be canceled. The major operational cost in this integrated process was the NaAc added to facilitate the denitrification in DR. Yet the 1.32 times dose versus theoretical demand was high-effective utilization and close to the previous study (Mokhayeri et al., 2009).

The current work provides a proof-of-concept of efficient remedy of complex mixed dye wastewater through retrofitting existing anaerobic/aerobic wastewater treatment processes with built-in BES. The treatment efficiency of the HAR + ABFR + DR integrated process was preferable compared to traditional process and the operational cost was reasonable. This result opens up the possibility of BES application to

printing and dyeing wastewater treatment, offering an economically viable solution to the dilemma of printing and dyeing wastewater treatment.

4. Conclusion

In this work, the integrated process consisting of the HAR, the ABFR, and the DR was developed to treat mixed dye wastewater well below the wastewater discharge standard. The HAR was demonstrated to be efficient in decolorizing mixed dyes (including azo dye, anthraquinone dye, and triarylmethane dye) under simulated practical scenarios for the first time. The DR position was identified as a vital factor, changing effluent COD and colority in the final effluent. The undesired autoxidation of decolorization intermediates could be mitigated by positioning DR after the ABFR.

CRediT authorship contribution statement

Min-Hua Cui: Conceptualization, Investigation, Writing - original draft. **Lei Gao:** Formal analysis, Validation. **Hyung-Sool Lee:** Conceptualization, Writing - review & editing. **Ai-Jie Wang:** Conceptualization, Supervision.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.biortech.2019.122420.

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