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Short Communication

Efficient azo dye wastewater treatment in a hybrid anaerobic reactor with a built-in integrated bioelectrochemical system and an aerobic biofilm reactor: Evaluation of the combined forms and reflux ratio

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ABSTRACT

A combined process that consisted of a hybrid anaerobic reactor (HAR) with an integral bioelectrochemical system and aerobic biofilm reactor (ABFR) was established for simulated azo dye wastewater treatment (domestic wastewater containing dye acid orange 7). The split combination form that separated HAR and ABFR into two individual reactors recorded a decolorization efficiency of 81.23 ± 0.12%, which was about 8% higher than that HAR and ABFR were stacked together into a single up-flow reactor. Implementation of reflux improved the decolorization and chemical oxygen demand (COD) removal in both the processes. Decolorization efficiency achieved 97.52 ± 0.66% in split process at a reflux ratio of 1 and the COD was 89 ± 2 mg/L in the final effluent. Further increasing the reflux ratio to 3 did not have any significance in treatment performance of the reactors. This study comprehensively revealed the influence of combination forms and reflux ratio on the performance of combined process.

1. Introduction

Textile printing and dyeing business are important supporting industries in China as well as in many other developing countries (Chen et al., 2011; Wang et al., 2018; Yang et al., 2018). According to the estimation by The World Bank, up to 20% of the discharged industry wastewater is from textile dyeing and finishing treatments (Kant, 2012). The unemployed dyes are major contributors in the discharged effluents of the textile printing and dyeing industries and those compounds probably trigger severe environmental issues, such as biological toxicity, "triple-induced" (carcinogenicity, teratogenicity, mutagenicity), unaesthetic appearance, etc. Azo dye is one of the largest consumption dyestuff categories around the world and characterized as possessing one or more azo bond (–N═N–) (Cui et al., 2016d). Particular structural feature of azo dyes essential for remaining stable under aerobic conditions, so anaerobic processes are vital for the efficient treatment of azo dye containing wastewater. However, the traditional anaerobic technologies in treating azo dye wastewater have bottlenecks such as low decolorization efficiency, time- consuming and difficulty in manipulating (Cui et al., 2016c).

The flourishing bioelectrochemical systems (BESs) technology provides a promising alternative to improve the performance of anaerobic processes. The BESs have been substantiated for enhancing various contaminants transformation, such as nitro-compounds (Shen et al., 2014), halogenated pollutants (Liang et al., 2019), sulfate (Blazquez et al., 2016), as well as azo dyes (Cui et al., 2017a). With a small applied external voltage (less than 1 V) on the electrodes, decolorization efficiency could be obviously increased within several hours. BESs still have many drawbacks towards scaling-up and real applications and the most efficient method is coupling them with conventional anaerobic units as hybrid reactors, rather than entirely replacing them. Both upflow and complete mixture anaerobic reactors have been successfully integrated with BESs (Cui et al., 2016a; Cui et al., 2016c). Nevertheless, the reduction intermediates, aromatic amine compounds, require subsequent aerobic mineralization. Very few studies have emphasized combination of anaerobic and aerobic processes in treating azo dye wastewater (Cui et al., 2014), though our previous literature focused on the feasibility instead of the parameter optimization.

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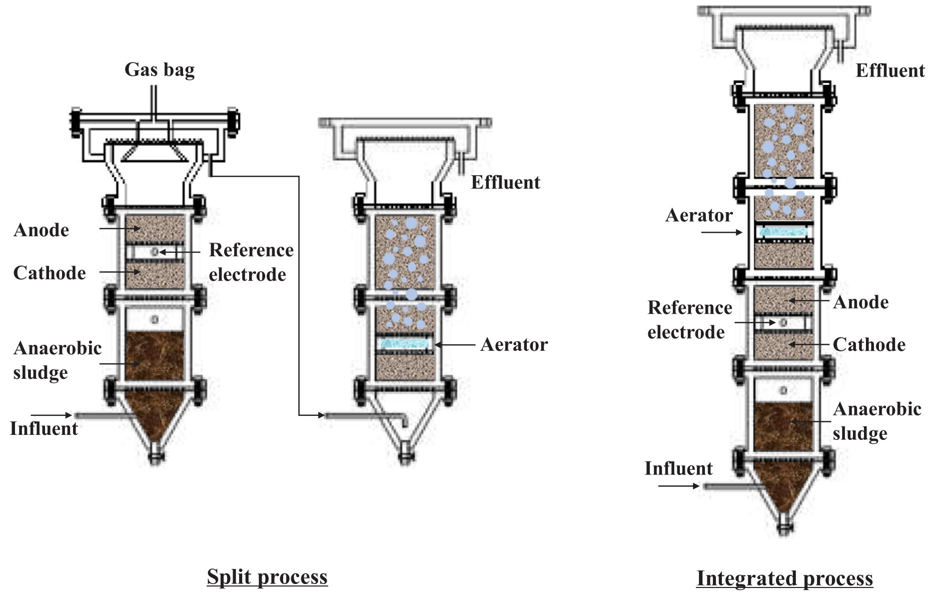

Fig. 1. Schematic of the split and integrated processes.

According to the aforementioned concerns, an anaerobic and bioelectrochemical hybrid bioreactor and an aerobic biofilm reactor were constructed and operated in the present study and the anaerobic and aerobic reactors were systematically evaluated. The influence of the reflux ratio on the performance of combined processes was also investigated.

2. Materials and methods

2.1. Reactor configuration

A hybrid anaerobic reactor (HAR) and an aerobic biofilm bioreactor (ABFR) were united in two modes, namely split process and integrated process, respectively, as shown in Fig. 1. The hybrid anaerobic bioreactor was a vertical tubular reactor and it was constituted of the anaerobic sludge at the bottom part and upper part with the bioelectrochemical system and had an empty volume of 1.25 L. Granular graphite (diameter from 3 to 6 mm, Linzhang county Deyuan carbon co., LTD, Handan, China) was used as both the anode and the cathode (8 cm in diameter and 4 cm in height) electrodes and a pair of electrodes were installed in the upper part of the reactor. The distance between the anode and the cathode was 2.5 cm, and the total volume of the electrodes was 200 cm^3. Prior to use, the granular graphite was pretreated by soaking it in 32% HCl solution for 24 h to remove inert materials. Graphite rod ($\Phi = 4$ mm) equipped at the electrode zone 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, and the electrode potential was monitored 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). An external resistance of 10 Ω was equipped in the external circuit to monitor electrode potential and voltage and the voltage across this resistor was recorded every 10 min with a data acquisition system (Keithley 2700, Keithley Co. Ltd., U.S.), which was 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 electrodes. 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.

2.2. Inoculation and operating conditions

Domestic wastewater was sampled from a local manhole of sewage pipe-line and it was amended with sodium acetate (NaAc, 1000 mg/L) and azo dye Acid Orange 7 (AO7) (200 mg/L), and the HAR in batch mode was operated using this amended wastewater as the substrate. The characteristics of the domestic wastewater used in this work were as follow: COD 273 ± 29 mg/L, total nitrogen 57.33 ± 5.98 mg/L, ammonium nitrogen 50.05 ± 5.04 mg/L, total phosphorus 8.36 ± 0.75 mg/L, pH 7.27 ± 0.12. When current-time profiles were replicated in batch cycles of operation, anaerobic sludge, that had been sampled from an up-flow anaerobic sludge blanket treating azo dye wastewater for more than six months, was added into the bottom of the HAR to stimulate hybrid biochemical reactions. After the batch operation for two more weeks, the HAR was switched to the continuous mode by feeding the amended wastewater with a peristaltic pump (BT100-1 L/YZ1515, Longer Pump Co., Ltd., China).

The ABFR was inoculated with the domestic wastewater collected from the local manhole. We supplemented the wastewater with electron donors to enrich the growth of heterotrophic aerobes. 1000 mg/L glucose was added to the domestic wastewater which was the substrate for the ABFR in batch mode during acclimation process. After COD removal reached steady-state, the batch operation of the ABFR was converted in continuous mode by feeding HAR effluent to the bioreactors in sequence with a peristaltic pump (BT100-1 L/YZ1515, Longer Pump Co., Ltd., China). The dissolved oxygen (DO) concentration in the ABFR was maintained at 2–4 mg/L by controlling the gas flowmeter during the experiments.

The experiment was divided into two stages. In stage 1, the influent azo dye AO7 concentration was fixed at 200 mg/L and the AO7 loading rates was increased from 200 to 960 g/(m^3·d) by decreasing the hydraulic retention time. In stage 2, the influent AO7 loading rate was fixed at 800 g/(m^3·d), the reflux ratio for HAR and ABFR were similar and was gradually increased from 0 to 3. The reflux ratio was controlled by a peristaltic pump (BT100-1 L/YZ1515, Longer Pump Co., Ltd., China). In this work, the liquid sample collected between anaerobic sludge layer and BES was labeled as “anaerobic sludge”, effluent of HAR was labeled as “BES” and the effluent of ABFR was labeled as “ABFR”.

2.3. Chemicals and analytical methods

Acid Orange 7 (AO7) was used as the model azo dye (purity > 95%, Shanghai Sangon Biotech Co., Ltd., China). The products of AO7 reduction were sulfanilic acid (SA) and 1-amino-2-naphthol (AN). In this study, SA (primary reagent, Aladdin Industrial Corporation) was used to calculate the product formation efficiency. All other chemicals were analytical reagents.

Liquid samples taken from reactors were immediately filtered through the 0.45 µm filters (Tianjin Jinteng Experiment Equipment Co., Ltd., China). AO7 concentration was quantified by a UV–Vis spectrophotometer (UV-1800, Shanghai Meipuda instrument Co., Ltd., China) at a wavelength of 484 nm. SA was measured by a high-performance liquid chromatography (HPLC, e2695, Waters Co., U.S.) equipped with a UV–Vis detector (model 2489, Waters Co., U.S.) and a C18 column (5 µm; 4.6 mm × 250 mm, Symmetry, Waters Co., Ltd., U.S.). To prevent the auto-oxidation of the products from AO7 reduction, 1000 mg/L Na_2SO_3 solution was added to dilute the liquid sample in a 1:1 ratio. Chemical oxygen demand (COD) was determined by using the HACH method. Data analysis was based on at least 5 samples from different HRTs in each steady state.

3. Results and discussion

3.1. Performance of combined processes at various azo dye loading rates

In order to evaluate the performance of two combined processes in treating simulated mixed azo dye wastewater, influent AO7 loading rate was increased from 200 to 960 g/(m^3·d), as shown in Fig. 2. Generally, two combined processes presented almost the same DE at lower AO7 loading rates (200 and 400 g/(m^3·d)). The difference occurred at higher AO7 loading rates and DE was 81.23 ± 0.12% in split process which was approximately 8% higher than that in integrated process at AO7 loading rate of 960 g/(m^3·d). It indicated that separating the HAR and ABFR into two individual reactors was preferable for AO7 decolorization than to stack them together when the influent AO7 loading rate higher than 600 g/(m^3·d). The previous study combining anaerobic sludge and carbon fiber brushes as a hybrid reactor presented 90.41 ± 6.20% decolorization efficiency at influent azo dye loading rate of 800 g/(m^3·d) (Cui et al., 2016b), which was similar to this work. The inferior performance of integrated process probably attributed to the undesired oxygen invasion that potentially influenced the bioelectrochemical performance of the BES module. When the anaerobic and aerobic processes separated in two reactors can provide strict oxygen free circumstances for HAR. The superior performance of split process was further justified by the AO7 decolorization rate in Fig. 2B. The maximum value of 779.81 g/(m^3·d) was observed in the split process at the influent loading rate of 960 g/(m^3·d). Regardless of the combined forms, anaerobic sludge decolorized most of the influent AO7, which accounted for more than 70% of total removed azo dyes in all conditions. The DE of the anaerobic sludge continuously decreased as the AO7 loading rate increased. The BES provided a whole new perceptible contribution to the overall decolorization process. Interestingly, on contrary with the decreased DE in anaerobic sludge, DE in BES was gradually increased from the AO7 loading rate elevated. The anaerobic sludge contacted the AO7 first and it was relatively easier to be affected by the toxicity of the dyes, while the BES served as a purifier which enhanced the DE deterioration of the entire HAR. The DE contribution of the ABFR unit was no more than 3% in all conditions. It has been authenticated by previous report that azo dye was quite stable under aerobic circumstances (Shaul et al., 1991).

The SA was one of the intermediates from AO7 reduction by azo bond cleavage (Cui et al., 2016d; Mu et al., 2009). SA concentration presented a similar trend with AO7 decolorization efficiency, implying that the reduction was the AO7 removal mechanism for both anaerobic sludge and BES, instead of adsorption, as shown in Fig. 3A. Theoretically, 1 mol AO7 reduction produced 1 mol SA, the SA recovery efficiency was calculated based on the calculation of measured and theoretical concentration, which was always higher than 86%. The effluent COD concentrations from each unit have been portrayed in Fig. 3B. Anaerobic sludge and ABFR removed most of the COD, and the

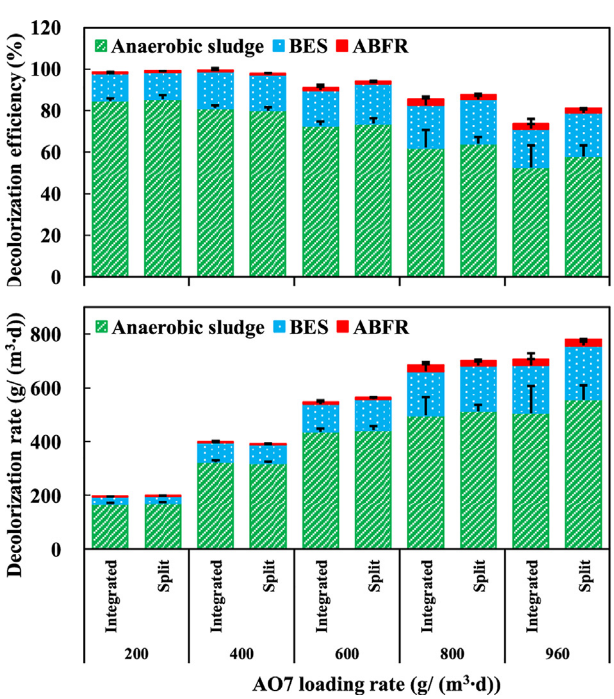

Fig. 2. Decolorization performance (A, decolorization efficiency; B, decolorization rate) of integrated and split processes at varying influent azo dye acid orange 7 loading rates. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

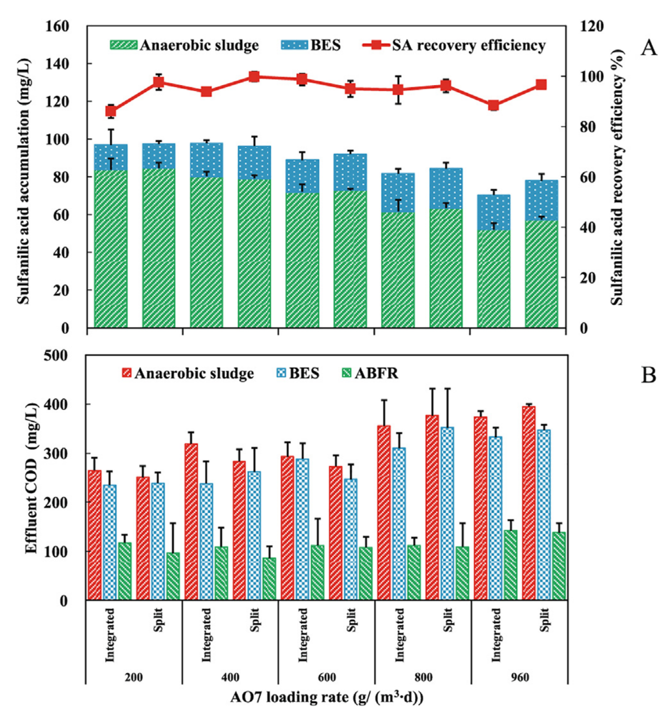

Fig. 3. The accumulation and recovery efficiency of sulfanilic acid (SA) (A) and effluent COD of different units (B) at varying influent azo dye acid orange 7 loading rates. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

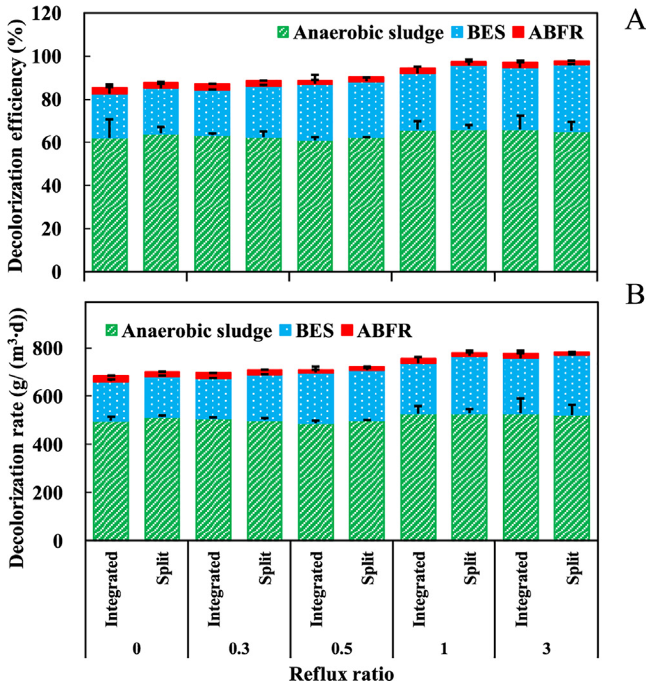

Fig. 4. Decolorization performance (A, decolorization efficiency; B, decolorization rate) of integrated and split processes at varying reflux ratios.

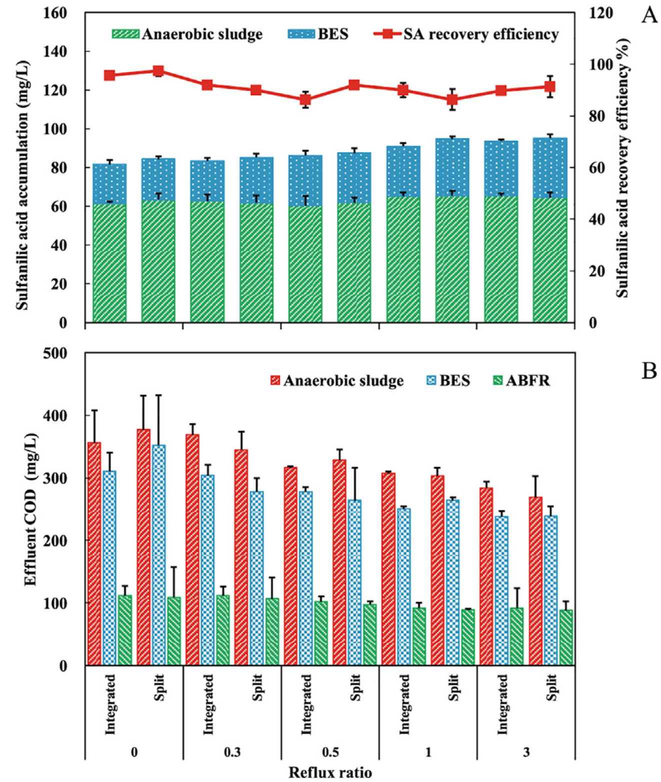

Fig. 5. The accumulation and recovery efficiency of sulfanilic acid (SA) (A) and effluent COD of different units (B) at varying reflux ratios.

contribution of BES was much lower as compared. The effluent COD concentrations from anaerobic sludge, demonstrated an increasing trend with the increase of influent AO7 loading rates and it was attributed to the stepwise increase of the influent AO7 concentration. Although these dyes were efficiently reduced to aromatic amines, they still cannot be completely mineralized under anaerobic conditions (Jonstrup et al., 2011). It can be inferred that the major reduced COD in anaerobic sludge was the biodegradable components from domestic wastewater. Although the effluent COD concentrations from HAR were continuously invigorating, ABFR presented increased COD removal performance and stable effluent COD concentrations (ranged from 86 ± 25 to 117 ± 17 mg/L) expect at highest influent AO7 loading rate of 960 g/(m^3·d). The influence of combined forms of HAR and ABFR on the COD removal was gradually reduced with increasing AO7 loading rates.

3.2. Effects of reflux ratio on the performance of integrated processes

The effluent reflux was conducted at the influent AO7 loading rate of 800 g/(m^3·d) to increase the treatment efficiency of combination processes. The effect of reflux ratio on the DE has been illustrated in Fig. 4A. The reflux was in accordance of the increasing DEs of both combined forms at all ratios and it was worth noticing that the dominated improvements were derived from the enhanced DE in BES instead of anaerobic sludge. DE of 97.52 ± 0.66% was observed in the split process at a reflux ratio of 1, which was 3% higher than the integrated processes. This decolorization performance was similar to the pure bioelectrochemical reactor treating AO7 under the same loading rate (Cui et al., 2016d). However, tripling the reflux ratio further improved DE to 97.23 ± 0.05% in integrated process and did not significantly increase DE in the split process (97.72 ± 0.15%), which was further proved by the decolorization rates in Fig. 4B. The AO7 decolorization rates increased with the reflux ratio increase from 0 to 3, which resulted in 777.84 and 781.76 g/(m^3·d) in integrated and split processes, respectively. It implied that the split process was desirable than integrated ones and could also achieve the maximum decolorization efficiency at the reflux ratio of 1, while the integrated process required a reflux ratio of 3 to obtain a similar performance. The lower reflux ratio demand foreboded lower power consumption, which would definitely influence the combined process choice in potential industrial applications in the future.

The decolorization product SA well accumulated in the effluent. The SA recovery efficiencies varied from 86.30 ± 3.16% to 97.40 ± 1.91% and this indicated that the azo bond reduction was the pathway for AO7 removal, as shown in Fig. 5A. With the sustained increase of reflux ratios, more organic content was removed in both HAR and ABFR, given a continuously decreased effluent COD concentration as shown in Fig. 5B. The intensified reflux ratio provided higher up-flow velocity that was benefit for mass transfer. Adequate mass transfer could enhance the anaerobic digestion process and improve the COD removal. The effluent COD (92 ± 9 and 89 ± 2 mg/L for the integrated and split process, respectively) from ABFR could be persistently below discharge standard for wastewater pollutions for dyeing and finishing of textile industry at the reflux ratio of 1. Further increasing the reflux ratio to 3 did not were not perceptibly enhance the COD removal efficiency.

The intensified decolorization and COD removal efficiency might be attributed to the enhancement of the bioelectrochemical reaction, as illustrated in Fig. 6. The potentials presented no obvious difference between the two combined forms and maintained steady values at all reflux ratio conditions. The anode potential varied from −288 ± 34 to −336 ± 9 mV, which was higher than the values reported in literatures as −400 to −500 mV (Cui et al., 2017b). It might be caused due to the insufficient supply of electron donor source from real domestic wastewater against the high concentration of electron acceptor AO7. The corresponding cathode potentials were in a range of −783 ± 28 to −832 ± 7 mV which was qualified for bioelectrochemical reduction of AO7. The current production from the individual process was significantly higher than that from the integrated process ($P = 0.021 < 0.05$) with the reflux ratio increased from 0 to 3. The current variation was in accordance with the decolorization and COD removal trend, and confirmed that the individual reactors can be more

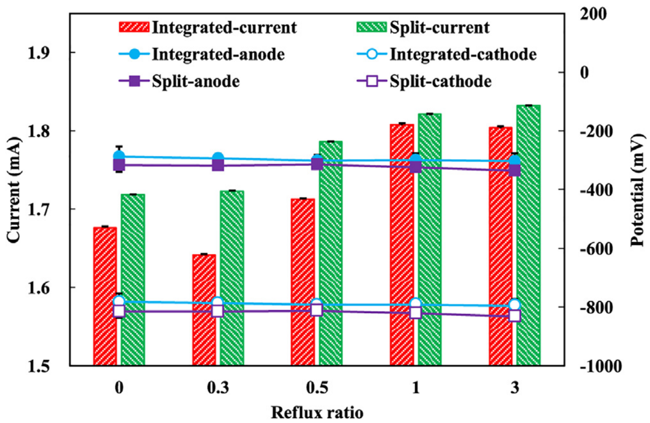

Fig. 6. Potentials and currents at varying reflux ratios.

compatible than the integrated ones.

3.3. Implications

This study successfully revealed the combination forms of HAR and ABFR on the dye wastewater treatment performance. Although vertically integrating these two reactors as one could minimize the process floor area, the inferior decolorization performance was the unconducive its application. Implementation of effluent reflux improved decolorization performance regardless of the combination forms. The split process reached the maximum decolorization performance at reflux ratio of 1, while the integrated process required higher reflux ratio to obtain similar performance. It implied the less power input in split process compared to integrated one. In the practical industrial application, the choice of the combination form and operating parameters should overall considerate the influent quality and discharge standard, limitation of facility floor area, and power consumption.

While the effect of two important factors, combination form and reflux ratio, were systematically explored in this work, more effort is required to bring BES technology closer to practical application. The feasibility of BES technology in treating practical dye wastewater, with complicated components (dyes from various categories), high salinity and pH, needs be evaluated. One or more integrated processes consisted of various units should be proposed to treat real dye wastewater fully meet the discharge standard. The hydraulic flow pattern analysis and the follow-up reactors configuration optimization are also the key factors to promote BES technology.

4. Conclusions

The azo dye (AO7) decolorization and COD removal efficiency of two integrated forms of a hybrid anaerobic reactor (HAR) and an aerobic biofilm bioreactor (ABFR) were compared. The split process where separation of HAR and ABFR in to two individual reactors was preferable than integrating HAR and ABFR into a single up-flow reactor. Implementing effluent reflux could increase the AO7 and COD removal efficiency, and a reflux ratio of 1 was the most effective and economical. These findings comprehensively revealed the effect of combined forms and reflux ratio on the decolorization efficiency and COD removal performance from dye wastewater, and illuminate the practical potential of this technology in wastewater treatment.

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