

Assessment of the Operational Parameters in Bioelectrochemical System in Perspective of Decolorization Efficiency and Energy Conservation

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Recently, bioelectrochemical systems (BESs) were investigated for enhancing recalcitrant contamination reduction of recalcitrant contaminants. However, comprehensive evaluation of key operational parameters considering both performance and energy conservation were rarely concerned. In this study, impact of the initial concentration, applied voltage and co-substrates types were thoroughly investigated and evaluated for optimization of Alizarin Yellow R (AYR) decolorization. Increase of the initial AYR concentration would decrease decolorization efficiency (DE) and rate (k), while change of applied voltage showed the contrary trend. However, the low unit energy consumption (UEC) demanded the high initial concentration ($1194 \text{ J}\cdot\text{g}^{-1}$ for $200 \text{ mg}\cdot\text{L}^{-1}$) and the low applied voltage ($112.4 \text{ J}\cdot\text{g}^{-1}$ for 0.1 V). k_{AYR} and k_{PPD} fed with glucose were almost twice than acetate, while, UEC was close or lower (the initial AYR under $100 \text{ mg}\cdot\text{L}^{-1}$ or applied voltage under 0.3 V), which indicated the superior property of glucose as co-substrate than acetate. The modeling proposed the optimized initial AYR concentration, applied voltage to guarantee the highest decolorization rate and the lowest energy consumption. The study proposed the experimental basis and technique approach to guide the operational parameter for scale-up BES application.

Keywords: Bioelectrochemical System (BES); Unit Energy Consumption (UEC); Decolorization; azo dye

1. INTRODUCTION

Recently, bioelectrochemical systems (BESs) have been gradually emerged for small molecule synthesis and the reductive transformation of various recalcitrant contaminants, including perchlorate, hexavalent chromium, nitro-aromatics, azo dye, halogenated aromatics and chloramphenicols [1-8]. Compared with the conventional biological approaches, BESs have shown enhanced reduction capacity with the low reduction potential caused by the biocathode through directly or indirectly electron transfer. The superior treatment capacity propose an alternative for advancing recalcitrant contaminants removal, which triggered a new upsurge of research in both the electron transfer related mechanism [9] and the scale-up feasibility [10].

Dyes are widely applied in textile, dyestuff and paper industries [11]. Each year, Millions of tons of dye-laden wastewater are generated in the world [12]. Among the various types of dyes, the contamination of azo dyes has constituted the largest chemical class of synthetic dyes discharged into environment [11, 13-15]. In 2009, Mu et al.[16] firstly reported the enhanced reduction of azo dyes in BES, and soon afterwards, the relevant studies have sprung up focusing on the accelerated decolorization feasibility under the different assembly systems [13, 17]. Practical applications for wastewater treatment were envisioned to be feasible for the development of modified BES configurations to satisfy the scale employment, including the membrane-free double-chamber BES [18], the integrated biocatalyzed electrolysis and bio-contact oxidation reactor [2], the assembled pilot-scale baffled reactor with the biocatalyzed electrolysis system [10], and the sleeve-type or cylindrical tube reactors [19].

However, all systems will face the similar or added challenges, which cover the balance of system performance and running cost, the two key factors are associated with the successful application of BES scaling-up. Efforts have been made to evaluate the influence on decolorization performance through some operational parameters, including the initial azo dye concentration, applied voltage [16, 20], co-substrates [21], the different reactor configuration [22] and etc. Mu et al. [16] and Cui et al. [20] reported the decreased initial concentration and the increased applied voltage would improve the decolorization efficiency. Also, the presence of extra organic carbon sources greatly increased color removal of azo dye compared to the control without extra organic carbon sources. Besides, another factor that could limit development of BES application is energy consumption by applied voltage [16]. The applied voltage determined both the decolorization performance and energy consumption. The higher applied voltage indicated the lower cathodic potential and the higher energy consumption. Mu et al. [16] reported the decolorization activities of azo dye, AO7, were significantly enhanced by controlling the cathodic potential in range of -350 to -550 mV vs SHE. As the potential increased, the decolorization efficiency was increased from 70.9 % to 98.7 %, and while, the consumed energy was also increased.

In fact, during operation, these key parameters were interrelated with each other, and could not be expounded separately [20]. However, so far, the research was lack of the comprehensive evaluation approach, which could systematically evaluate considering both decolorization performance and energy conservation [16, 20]. How the operational parameters influence the consumed energy and decolorization performance and under which condition both the high performance and the low energy

consumption could be stably maintained, are remaining questions. Decolorization efficiency (DE) and rate (dynamic response constant k) could be applied to evaluate the system performance and the unit energy consumption (UEC) could be applied to estimate the consumed energy brought by the applied voltage.

In this study, the initial concentration of pollutant, applied voltage and co-substrates to both treatment efficiency and energy consumption were thoroughly evaluated in dual-chambered azo dye reductive decolorization BESs. One typical azo dye, alizarin Yellow R (AYR), which contained a single azo bond and regarded as one of the most widely applied type of azo dye, was selected as the aim pollutant in this study [23, 24]. The parameters were modeled considering DE, k and UEC, and the optimized operational conditions were provided. Aims of the study were to verify the impact of some vital operational parameters on both the efficiency and energy consumption and provide a comprehensive evaluation approach/model to guarantee the low running cost during the enhanced reduction of recalcitrant contaminants in BESs.

2. MATERIALS AND METHODS

2.1. BES construction, operation and medium composition

Dual-chamber BESs were separated by a cation exchange membrane (5 cm in diameter) (CEM, Ultrex CMI-700, Membrane International, U.S.) with the working volume in each chamber of 80 mL. Carbon brushes with diameter of 4.5 cm and length of 4 cm (TOHOTENAX Co. Ltd.) were applied as the working electrode in cathode and the reference electrode in anode. A saturated calomel electrode (SCE, +247 mV vs. Standard hydrogen electrode, SHE, Shanghai Precision Scientific Instruments Co. Ltd, China) was placed in the cathode chamber to measure the electrode potentials. Reactors were running in closed circuit mode using a DC power (IT6921, Itech Co. Ltd., USA) and with the external resistance of 20 Ω . Data of electrode potentials and current were collected every ten minutes using a data acquisition (Keithley 2700, Keithley Co. Let., USA). The system was sealed to maintain the anaerobic condition. All tests were performed at the room temperature (25 °C).

Compositions of artificial wastewater supplied in cathode and anode chamber were as follows ($\text{g}\cdot\text{L}^{-1}$): $\text{Na}_2\text{HPO}_4\cdot 12\text{H}_2\text{O}$: 11.55; $\text{NaH}_2\text{PO}_4\cdot 2\text{H}_2\text{O}$: 2.77; NH_4Cl : 0.31; KCl : 0.13. Other than this, cathode was additionally applied with glucose ($1\text{ g}\cdot\text{L}^{-1}$) or sodium acetate ($1\text{ g}\cdot\text{L}^{-1}$) as extra carbon source (electrons donors), and AYR was applied as the objective pollutant [20]. All reactors were inoculated with 10 mL of activated sludge (total suspended solids of $15695 \pm 260\text{ g}\cdot\text{L}^{-1}$; soluble carbohydrate of $35 \pm 5\text{ mg COD}\cdot\text{L}^{-1}$) collected from Taiping wastewater treatment plant (Harbin, China)[25]. All reactors were simultaneously constructed with two parallel reactors holding the same condition. The applied AYR concentration was ranged from 25, 50, 100, 150 and 200 $\text{mg}\cdot\text{L}^{-1}$ (the applied voltage was set at 0.5V), and the applied voltage was ranged from 0, 0.1, 0.3, 0.5 and 0.7 V (the initial AYR concentration was set at 100 $\text{mg}\cdot\text{L}^{-1}$). All those results obtained under steady state after continuous running for 30 days were reported here.

2.2. Chemical analysis and statistical analysis

Liquids were sampled and immediately filtered through a 0.45 μm membrane. AYR was measured using a UV-visible spectrophotometer (UV-1800 spectrophotometer, MAPADA Incorporation, Shanghai, China) at a wavelength of 374 nm. The decolorization products of AYR, including the two main decolorization products of p-phenylenediamine (PPD) and 5-aminosalicylic acid (5-ASA), were measured using HPLC (Waters mode e2695, Waters Incorporation, USA) equipped with a Water Symmetry C18 column (5 μm ; 4.6 \times 250 mm, Waters Incorporation, USA) at 35 $^{\circ}\text{C}$ and a UV/visible detector (model-2489, Waters Incorporation, USA) at 288 nm and 368 nm, respectively. The applied mobile phase was methanol/ H_2O (containing 0.03 % acetic acid) (8:2) at a flow rate of 1.0 $\text{mL}\cdot\text{min}^{-1}$. The retention time of PPD and 5-ASA were 2.101 and 3.021 mins, respectively.

AYR decolorization efficiency (DE) was calculated by the removed AYR concentration divided by the initial AYR concentration; Current (I) was calculated applying Ohm's law by connection of the external resistance (20 Ω); Electron recovery efficiency (ERE_{AYR}) was based on the cathode AYR reduction; Unite Energy consumption (UEC: $\text{J}\cdot\text{g}^{-1}$ AYR) was calculated with the power cost. The detailed calculation methods of DE, I, ERE_{AYR} and UEC were described as shown in the following equations (1) to (4) [16]:

$$DE = \frac{C_{\text{in-AYR}} - C_{\text{eff-AYR}}}{C_{\text{in-AYR}}} \times 100\% \quad (1)$$

$$I = \frac{U_R}{R} \quad (2)$$

$$\text{ERE}_{\text{AYR}} = \frac{10 \times \frac{(C_t - C_0) \times V_{\text{Cathode}} \times F}{M_{\text{AYR}}}}{\int_0^t I dt} \times 100\% \quad (3)$$

$$\text{UEC} = \frac{U \times \int_0^t I dt}{(C_t - C_0) \times V_{\text{Cathode}}} \quad (4)$$

Where $C_{\text{in-AYR}}$ is the influent AYR concentration, $\text{g}\cdot\text{L}^{-1}$; $C_{\text{eff-AYR}}$ is the effluent AYR concentration, $\text{g}\cdot\text{L}^{-1}$; U_R is the voltage of R (20 Ω); I is the current in the circle of the reactor, A; U is the applied voltage, 0.5 V; t is time, h; V_{cathode} is the effective volume of cathode-chamber (L); M_{AYR} is the molecular weight of AYR, 287.20 $\text{g}\cdot\text{mol}^{-1}$; F is Faraday's constant (96,485 $\text{C}\cdot\text{mol}^{-1}\cdot\text{e}^{-1}$). The rates of AYR reduction and PPD formation were fitted using an apparent first-order reaction model: $C = C_0 e^{-k_{\text{AYR}} t}$ and $C = C_0 (1 - e^{-k_{\text{PPD}} t})$ [26], respectively, where C represent AYR or PPD concentration ($\text{mg}\cdot\text{L}^{-1}$) at time t (h). C_0 is the initial AYR concentration or maximum PPD production concentration. The rate constant k (h^{-1}) was calculated using SigmaPlot V12.5. The significant factors identified from initial AYR concentration ($\text{mg}\cdot\text{L}^{-1}$), applied voltage (V) and time (h) were arranged as independent variables. Decolorization efficiency (DE, %), the first-order dynamic response constant (k , h^{-1}) and unit energy consumption (UEC, $\text{J}\cdot\text{g}^{-1}$) was taken as the response variables, and a second-order polynomial function was used to connect the independent variables and the response. The Design Expert (Version 8.0.6.1, Stat-Ease Inc, Minneapolis, MN, USA) software was used for regression and graphical, analyses of the data obtained. The interactive effects of the independent variables on the dependent ones were illustrated by three- and two- dimensional contour plots. All experimental designs were randomized, and mean values were applied.

3. RESULTS AND DISCUSSION

3.1. Reductive decolorization under the different AYR initial concentration

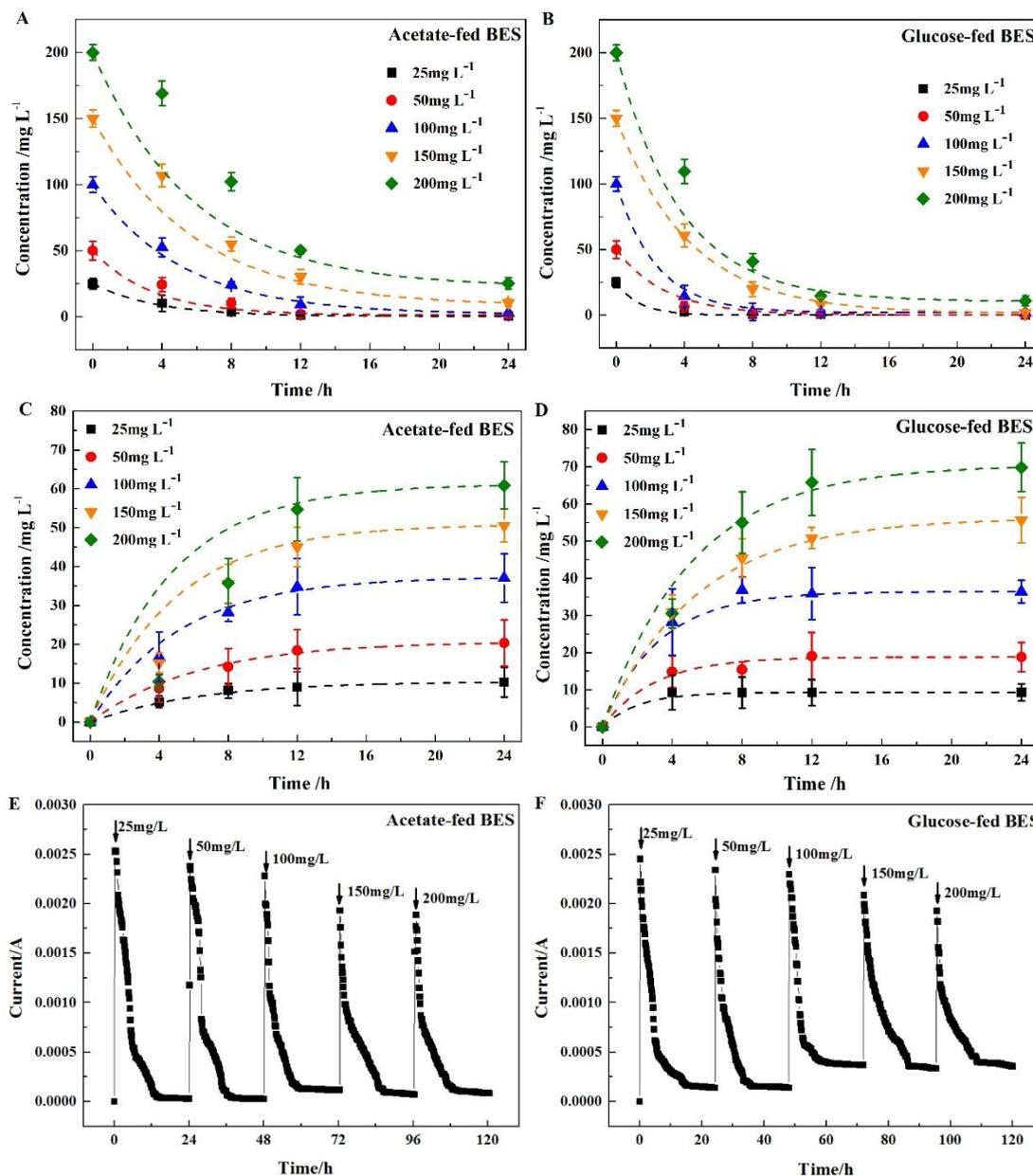


Figure 1. Effects of the initial AYR concentration for AYR decolorization with the external voltage of 0.5 V and AYR concentration ranged from 25, 50, 100, 150, 200 mg·L⁻¹, respectively, in dual chamber BESs at the steady running state. (A) and (B): AYR reductive decolorization fed with acetate and glucose as carbon source, respectively; (C) and (D): PPD generation as AYR was decolorized fed with acetate and glucose as carbon source, respectively; (E) and (F): Current changes during AYR reductive decolorization fed with acetate and glucose as carbon source, respectively. All data were obtained as the mean values with triplicate parallel samples.

Blank experiments showed AYR adsorption to electrode and sludge could be completely neglected under conditions either supplying the different initial AYR or the different voltage. With the

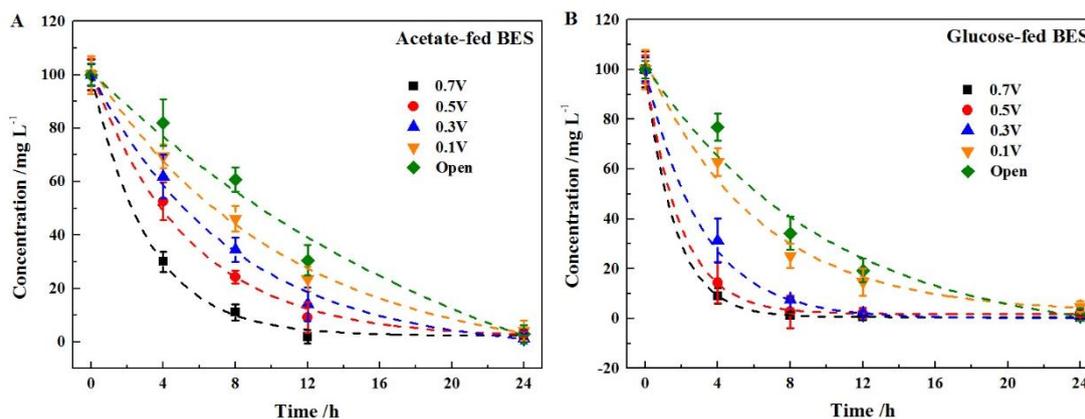
applied voltage of 0.5 V, AYR could be stably removed after 24 h under the different initial concentration (Fig. 1A and B). DEs was more than 80% in 4 h as the initial concentration was less than $100 \text{ mg}\cdot\text{L}^{-1}$. DE decreased as the increase in AYR initial concentration. When AYR concentration increased from 25 to $200 \text{ mg}\cdot\text{L}^{-1}$, DE in 4 h decreased from 59.3 to 15.5 %. Also, with the same initial AYR concentration DE was 89.3 ~ 45.2 % higher if glucose was co-substrates, than that with acetate.

Two main products are generated during AYR decolorization, which are PPD and 5-ASA. As the previous report, recovery efficiency of PPD can be achieved at around 99 %; in comparison, 5-ASA is rather instable, and tended to be further degraded by anaerobic bacteria [2, 27]. Therefore, PPD was selected as the representation of decolorization metabolites in this study. As shown in Fig. 1C and D, after 24 h, the highest recovery rate of PPD approached nearly 100 % with both acetate and glucose as co-substrates, indicating the complete decolorization of AYR. However, the PPD generation efficiency showed the similar trend with that of DE of AYR. For example, when the initial concentration increased from 25 to $200 \text{ mg}\cdot\text{L}^{-1}$, PPD generation efficiency in 8h decreased from 32.3 to 17.9 % (acetate-fed BES) and 37.0 ~ 27.5 % (glucose-fed BES), respectively. Also, PPD generation efficiency was a little higher under conditions with glucose than that of acetate.

With both glucose and acetate as co-substrates, the current decreased sharply as soon as AYR decolorization in the initialed and trended to be stable after 12 h (Fig. 1E and F). This indicated the cathodic involved in AYR decolorization process. However, no obvious decrease was occurred as the initial AYR concentration increased.

3.2. Reductive decolorization under the different external voltage

Under the fixed initial concentration ($100 \text{ mg}\cdot\text{L}^{-1}$), AYR decolorization efficiency was enhanced as the applied voltage improved from 0.1 to 0.7 V, supplying either acetate or glucose as co-substrates (Fig. 2A and B). The open circuit and 0.1V of applied voltage (cathode potential of -500 mV and -600 mV), resulted in a much slower decomposition capacity, possibly caused by the low reducing environment which made $-\text{N}=\text{N}-$ azo bond difficult to be decomposed [16, 20]. Generally, BES supplied with glucose showed the higher DE than acetate under the same voltage. For example, under 0.7 V of external voltage, 90.9 % and 69.9 % of DE were obtained within 4 h supplied glucose and acetate as co-substrates, respectively.



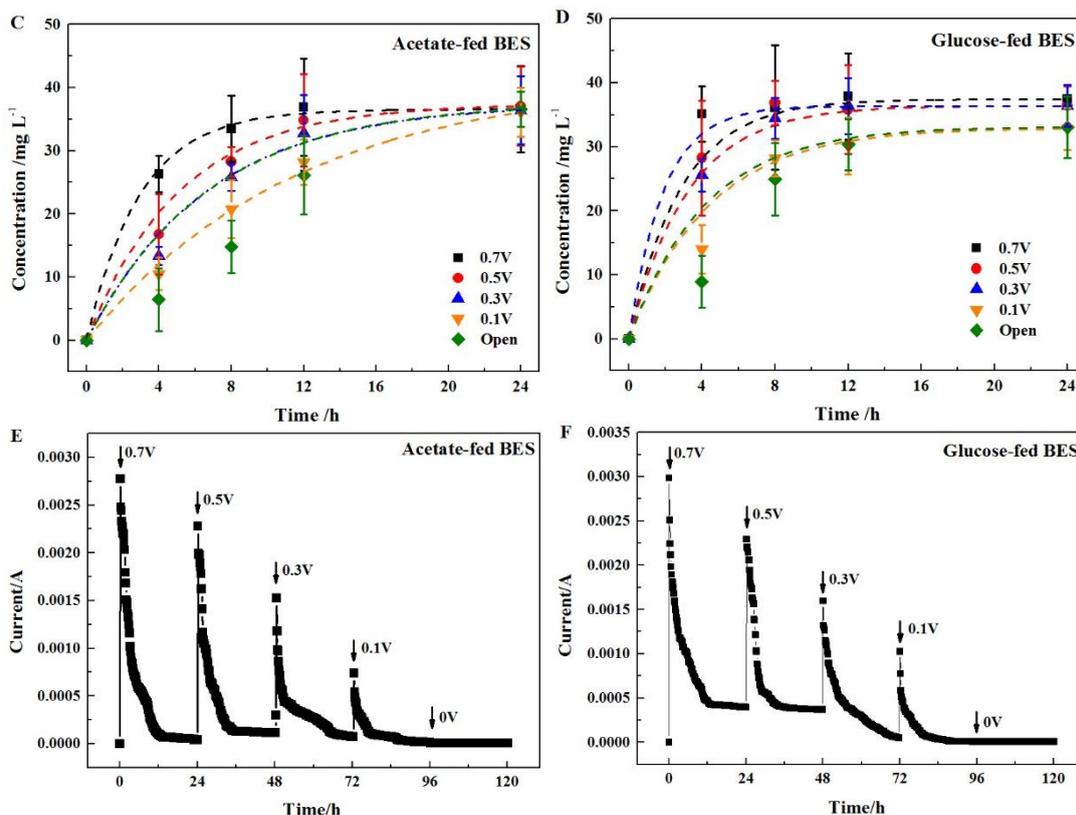


Figure 2. Effects of the applied voltage for AYR decolorization with the initial AYR concentration of $100 \text{ mg}\cdot\text{L}^{-1}$ and the external voltage ranged from 0, 0.1, 0.3, 0.5 and 0.7 V, respectively, in dual chamber BESs at steady state. (A) and (B): AYR reductive decolorization fed with acetate and glucose as carbon source, respectively; (C) and (D): PPD generation as AYR was decolorized fed with acetate and glucose as carbon source, respectively; (E) and (F): Current changes during AYR reductive decolorization fed with acetate and glucose as carbon source, respectively. All data were obtained as the mean values with triplicate parallel samples.

PPD generation tendency was coincident with DE of AYR. Glucose fed condition showed the higher recovery rate than acetate fed one; the generation efficiency was increased as the external voltage supply improved (Fig. 2C and D). The generation efficiency was gradually increased to 35.1 % (glucose-fed) and 26.3 % (acetate-fed) as the applied voltage increased from 0 V to 0.7 V. About 33.5 % of increase was observed under conditions fed with glucose than fed with acetate.

The current decreased sharply as soon as AYR decolorization started, indicated the electron transfer in cathode correlated with AYR decolorization (Fig. 2E and F). Also, the current changed largely (from 3 mA to 1 mA for glucose and from 2.5 mA to 0.5 mA for acetate, respectively) as the applied voltage varied from 0.7 V to 0.1 V.

3.3. Interrelations of the initial concentration and external voltage with k , UEC and ERE_{AYR}

Under all of the conditions, rates of AYR decolorization and PPD generation fitted well with the first-order kinetics, with R values over 0.98. Figure 3 A and B gave the dynamic response constant (k) under the different AYR initial concentrations and applied voltages, respectively. It was noticed,

k_{AYR} and k_{PPD} were almost twice that with glucose as co-substrates than with acetate, by applying either the different initial concentration or the external voltage.

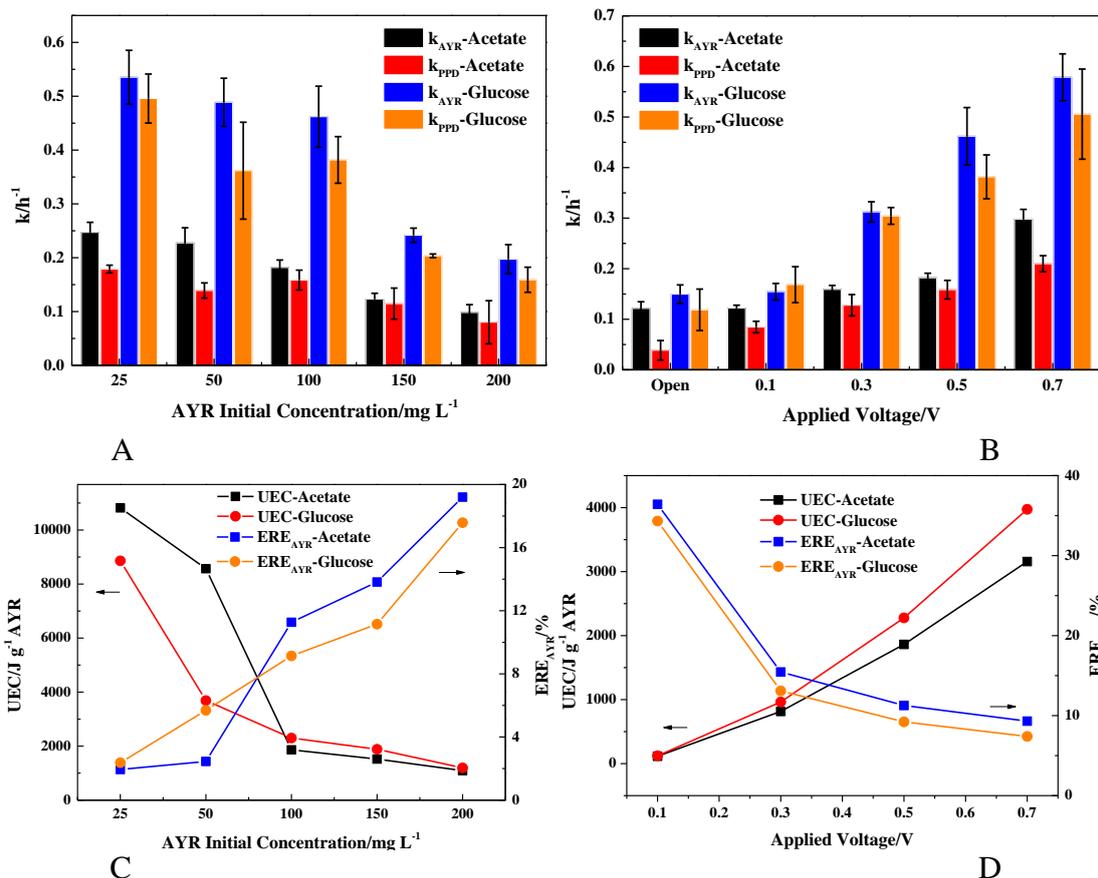


Figure 3. The respective k_{AYR} , k_{PPD} fitting with the first-order kinetics, under the different initial AYR concentration (A) and applied voltage (B) with respective acetate and glucose as carbon sources; unit energy consumption (UEC) and energy recovery efficiency (ERE_{AYR}) under the different initial AYR concentration (C) and applied voltage (D) with respective acetate and glucose as carbon sources.

Both the AYR decolorization rate and PPD generation rate were gradually decreased as the initial AYR concentration gradually increased. The k_{AYR} ranged from 0.247 to 0.098 h^{-1} (acetate-fed BES) and 0.535 to 0.197 h^{-1} (glucose-fed BES), and while, k_{PPD} ranged from 0.496 to 0.159 h^{-1} (acetate-fed BES) and 0.506 to 0.119 h^{-1} (glucose-fed BES), when AYR initial concentration increased from 25 to 200 $mg \cdot L^{-1}$. Also, both AYR decolorization rate and PPD generation rate were gradually increased as the supplied voltage improved. The k_{AYR} increased from 0.121 to 0.298 h^{-1} (acetate-fed BES) and 0.149 to 0.579 h^{-1} (glucose-fed BES), while k_{PPD} ranged from 0.119 to 0.506 h^{-1} (acetate-fed BES) and 0.039 to 0.209 h^{-1} (glucose-fed BES), when the applied voltage increased from 0.1 to 0.7V.

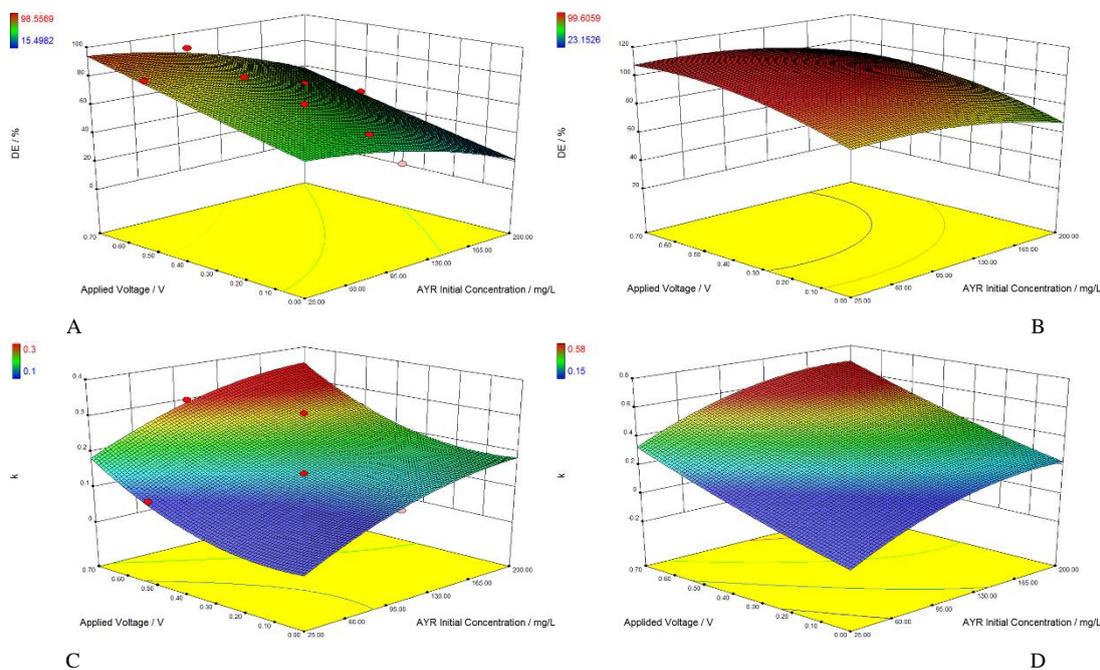
Within 12 h, current changes, UEC and ERE_{AYR} under the different applied voltage during AYR decolorization were shown in Fig. 3C and D. As AYR concentration increased from 25 to 200 $mg \cdot L^{-1}$, UEC was gradually decreased from 10820.8 to 1093.5 $J \cdot g^{-1}$ (acetate-fed BES); from 8859.6 to

1194.7 J·g⁻¹ (glucose-fed BES), suggested the more efficient utilization of electrons, although the decolorization rate represented a gradual decrease trend (Fig. 3A). UEC was higher with acetate than that with glucose when the initial concentration was less than 100 mg·L⁻¹, however, it became lower as the initial concentration over 100 mg·L⁻¹. As the applied voltage increased from 0 to 0.7 V, UEC was gradually increased to 3156.9 J·g⁻¹ (acetate-fed BES) and 3973.2 J·g⁻¹ (glucose-fed BES), respectively. This was probably attributed to the more energy (current) involvement in decolorization process. Under 0.3 V, UEC was close with either acetate or glucose, and however, it became higher with glucose than acetate as the applied voltage further increased.

ERE_{AYR} represented the different trend with that of UEC. As the initial concentration increased from 25 to 200 mg·L⁻¹, ERE_{AYR} was gradually increased from 1.94 to 19.20 % (acetate-fed BES) and 2.37 to 17.58 % (glucose-fed BES), indicating the more electrons participated. As the applied voltage was increased from 0.1 to 0.7 V, ERE_{AYR} was gradually decreased from 36.41 to 9.31 % (acetate-fed BES) and 34.32 to 7.40 % (glucose-fed BES), indicating the accumulation of unemployed electrons. Under the same voltage, ERE_{AYR} was lower with acetate than that with glucose when the initial concentration was less than 100 mg·L⁻¹, however, it became higher as the initial concentration over 100 mg·L⁻¹. ERE_{AYR} with acetate was higher than that with glucose under the different voltage supplement.

3.4. Modelling the key parameters for optimization of DE and UEC

Models corresponding to DE (%), *k* (h⁻¹) and UEC (g·J⁻¹), were quantitatively evaluated with the independent variables, including the initial AYR concentration (A), applied voltage (V) and time (h), according to the results presented in Fig. 3. Investigated results of the correlations were described on quadratic equations listed in supplementary information (SI).



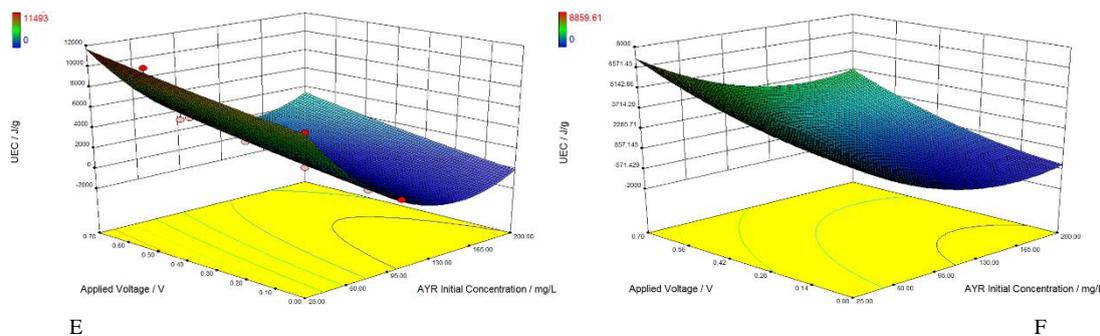


Figure 4. The response surface plots showing the effects of initial AYR concentration and applied voltage on (A) and (B): the decolorization efficiency (DE); (C) and (D): the dynamic response constant (k); (E) and (F): the unite energy consumption (UEC) in 12 h, with acetate and glucose as carbon source, respectively.

The corresponding response surface plots according to the models (SI, equation 1-6) over the interactive variables of the initial AYR concentration (25 ~ 200 mg L⁻¹) and applied voltage (0 ~ 0.7 V), were shown in Fig. 4. DE of the AYR under acetate-fed BES was more sensitive to the initial AYR concentration and applied voltage than glucose-fed BES. The fitting data of DE was ranged between 98.6 ~ 15.5% (acetate-fed BES) and 99.6 ~ 23.2% (glucose-fed BES), respectively (Fig. 3A and B). The glucose-fed BES of k_{AYR} was higher than acetate-fed BES, that ranged between 0.3 ~ 0.1 h⁻¹ (acetate-fed BES) and 0.58 ~ 0.15 h⁻¹ (glucose-fed BES), respectively (Fig. 3C and D). The fitting data of UEC_{max} was 11493 J·g⁻¹ (acetate-fed BES) and 8859.6 J·g⁻¹ (glucose-fed BES), which indicated glucose consume lower energy per gram of AYR.

The optimized initial AYR concentration and applied voltage, and the corresponding expected DE, k_{AYR} and UEC after optimization, were shown in Table 1.

Table 1. Optimized operational conditions of the initial AYR concentration and applied voltage and the suggested values of DE, k_{AYR} and UEC with both acetate and glucose as co-substrates

Carbon source	Initial AYR concentration (mg·L ⁻¹)	Applied voltage (V)	Decolorization efficiency (DE) (%)	k_{AYR} (h ⁻¹)	UEC at 12 h (J·g ⁻¹)	Desirability (%)
Acetate	130~135*	~0.66	~93.44	0.30~0.32	1639~1790	93
Glucose	~155	~0.58	~99.60	~0.58	2256.8	90.7

*: all data was obtained based on the optimized calculation the response surface plots and quadratic model analysis.

It is noticed both of the demanded initial concentration demand and impressed voltage were similar for applying acetate and glucose. The required initial concentration of acetate (~ 130 mg·L⁻¹) was lower than that of glucose (~ 155 mg·L⁻¹), and however, the voltage demand (~ 0.66 V) was higher than that with glucose (~ 0.58 V). Under that condition, the obtained decolorization rate (k) was

much quicker with glucose than that with acetate, however, the higher energy consumption was required, although both of them achieved over 93% of the decolorization efficiency after 12 h.

3.5. Discussion

The study firstly detailed described the interrelations between the key operational parameters and system performance (DE, k , and UEC) during the enhanced reduction in BES. Although BESs showed the superior decolorization capacity, that most of the applied AYR could be completely removed within 24 h and the optimal PPD recovery rate were obtained (Fig. 1 and 2). DE, k , UEC and ERE_{AYR} represented the remarkable diverse tendency under the different initial concentration and applied voltage (Fig. 3). This contradiction on performance and energy consumption would significantly affect operation and performance during scale-up study, therefore, the identification of their interrelationships is vital. The initial AYR concentration increased resulted in the decrease of DE, k and UEC and the increase of ERE_{AYR} . The higher initial AYR concentration would inhibit the activity of cathodic microorganism which result in the slower reaction speed because of its toxicity [28]. However, the high initial AYR concentration was recommended in view of energy conservation. As the applied voltage increased, DE and k were largely improved, attributing to the more reducing environment brought by the negative cathode potential [20]. However, the higher applied voltage drove the high energy consumption.

The study suggested the optimized operational conditions that allowed the highest decolorization efficiency and rate reached 93.4 % and 0.32 h^{-1} for acetate and 99.6 % and 0.58 h^{-1} for glucose, respectively, through the modeling studies (Fig. 4 and Table 1). Also, UEC were $1639 \sim 1790 \text{ J}\cdot\text{g}^{-1}$ for acetate and $2256.8 \text{ J}\cdot\text{g}^{-1}$ for glucose, respectively. Previously, Sun et al. [29] reported the reductive decolorization of Congo red, with the highest DE of about 86 % in algae-contained BES supplying glucose after 24 h. Liu et al. [30] focused on decolorization of Reactive Brilliant Red X-3B, with DE of about 40 % and 60 % under 0.5 V and 1 V of external voltage supply. Power consumption was 0.21 mW (about $4910 \text{ J}\cdot\text{g}^{-1}$ of UEC after unit conversion). Sun et al. [5] reported the decolorization of AYR in the plug-flow baffled BES. DE approached to 93.5 % with 0.5 V of external applied voltage and the UEC was reported as $1305 \text{ J}\cdot\text{g}^{-1}$. Compared with the above studies, the optimized performance in this study possessed the superior advantages in both the decolorization efficiency and energy conservation.

During azo dye decolorization, co-substrates are essential as both carbon source and potential electron donors [20, 21, 31]. It was noticed, glucose-fed system demanded the low impressed voltage than acetate, and whereas, the obtained decolorization rate was much quicker than that with acetate (Fig. 1, 2 and 3). This indicated glucose was more efficient as electron donor in faster conversion of the co-substrate to produce more electrons, consistent with the pervious report by Sun et al. [21].

Besides these operational parameters, system configuration was another factor that would impact the system performance. Previously, many studies have been focused on the treatment efficiency by the modified configuration BES, through removing the membrane, modifying the electrode, or integrating/assembling with other bioreactors [4,18,19,32,33]. However, the energy

consumed after configuration modification has been rarely reported. Further study correlated with the energy conservation and treatment efficiency for configuration modified system is warranted, to further explore the cost-effective solutions of the scale-up studies during the effective removal of the toxicity of recalcitrant contaminants.

4. CONCLUSION

Briefly, the study comprehensively investigated and evaluated the key operational parameters, including the initial concentration, applied voltage and co-substrates types (acetate and glucose) in BESs for enhanced decolorization of AYR. After optimization, appropriate conditions for the AYR initial concentration and applied voltage were suggested as $\sim 130 \text{ mg}\cdot\text{L}^{-1}$ and 0.66 V for acetate-fed system, and $\sim 155 \text{ mg}\cdot\text{L}^{-1}$ and 0.58 V for glucose-fed system, respectively. Meanwhile, the high decolorization efficiency, rate (93.4 % and 0.32 h^{-1} for acetate; 99.6 % and 0.58 h^{-1} for glucose) and the low energy consumption ($1639 \sim 1790 \text{ J}\cdot\text{g}^{-1}$ for acetate; $2256.8 \text{ J}\cdot\text{g}^{-1}$ for glucose) were guaranteed. The study gave valid suggestions on parameter design for scale-up BES studies.

SUPPLEMENTARY DATA:

3.4. Modelling the key parameters for optimization of DE and UEC

Models corresponding to DE (%), k (h^{-1}) and UEC ($\text{g}\cdot\text{J}^{-1}$), were quantitatively evaluated with the independent variables, the initial AYR concentration (A), applied voltage (V) and time (h), according to the results presented in Fig.3.

Investigated results of the correlations were described on quadratic equations listed as below (equations 5-7: fed with acetate; equations 8-10: fed with glucose).

$$\begin{aligned} \text{DE}_{\text{acetate}} = & +63.59-17.42\times A+18.78\times B+23.77\times C \\ & +3.27\times A\times C-4.38\times B\times C-6.26\times A^2+0.62\times B^2-3.87\times C^2 \end{aligned} \quad (1)$$

$$\begin{aligned} k_{\text{acetate}} = & +0.16+0.084\times A+0.084\times B+0.000\times C \\ & +0.000\times A\times C+0.000\times B\times C-0.036\times A^2+0.057\times B^2-0.000\times C^2 \end{aligned} \quad (2)$$

$$\begin{aligned} \text{UEC}_{\text{acetate}} = & +763.33-4117.64\times A+1769.78\times B-140.52\times C \\ & -90.15\times A\times C-31.76\times B\times C+4853.83\times A^2+166.81\times B^2-20.82\times C^2 \end{aligned} \quad (3)$$

$$\begin{aligned} \text{DE}_{\text{glucose}} = & +101.87-7.86\times A+12.11\times B+18.05\times C \\ & +8.87\times A\times C-14.28\times B\times C-6.33\times A^2-7.84\times B^2-16.98\times C^2 \end{aligned} \quad (4)$$

$$\begin{aligned} k_{\text{glucose}} = & +0.36+0.18\times A+0.23\times B+0.000\times C \\ & +0.000\times A\times C+0.000\times B\times C-0.10\times A^2+0.026\times B^2-0.000\times C^2 \end{aligned} \quad (5)$$

$$\begin{aligned} \text{UEC}_{\text{glucose}} = & +1250.57-1729.68\times A+1998.45\times B+353.54\times C \\ & +827.83\times A\times C+444.76\times B\times C+1597.23\times A^2+640.05\times B^2-428.93\times C^2 \end{aligned} \quad (6)$$

Where A, B and C represented the independent variables of the initial AYR concentration ($\text{mg}\cdot\text{L}^{-1}$), voltage (V) and time (h), respectively.

F-value and P-value for each variable in the quadratic model are presented in Table S1. Analysis of variance was conducted to test the significance of fit of DE, k and UEC, respectively. All of the values of 'Prob > F' are less than 0.0001, indicating that the model terms were significant. The corresponding F-values were 215.56, 89.17 and 85.53, respectively, fed with acetate, and 37.89, 159.42 and 9.10, respectively, fed with glucose. Therefore, equations (1) to (6) corresponding well with the predicted values of DE, k and UEC, and these quadratic models could be used to navigate the design space.

Table S1. F- and P-value for the quadratic models (second-order polynomial equation)

Source	Sum of squares	df	Mean square	F value	p-value Prob > F
equation (1)	23464.52006	8	2933.065008	215.55757	< 0.0001
equation (2)	0.165948524	8	0.020743565	89.170446	< 0.0001
equation (3)	407491880.2	8	50936485.02	85.534288	< 0.0001
equation (4)	11645.99052	8	1455.748815	37.887459	< 0.0001
equation (5)	0.969865266	8	0.121233158	159.41762	< 0.0001
equation (6)	118682727.6	8	14835340.95	9.0984404	< 0.0001

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