



Simultaneous ammonium and colour removal from digested piggery wastewater for *Arthrospira* cultivation by coupling micro-electrolysis and cation exchange membrane

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ABSTRACT

A coupling device integrated with the advantages of Fe-C micro-electrolysis and cation exchange membrane systems was successfully designed and operated for pretreatment of *Arthrospira* cultivation with digested piggery wastewater (DPW). In this coupling device, cation exchange process and Fe-C micro-electrolysis process are promoted mutually, and obtained better treatment efficiency than single system on ammonium, colour and total organic carbon (TOC). Specifically, it removed 77 % of NH_4^+ , 83 % of NO_2^- , 92 % of colour and 62.5 % of TOC with the residual corresponding concentration of 51.9 mg/L, 50.6 mg/L, 79 mg-Pt/L and 47.4 mg/L, respectively. As these toxic contaminants were removed to a satisfied level, nitrate, the safest nitrogen source for *Arthrospira*, was retained approximately 72%. Thus, the cultivation of *Arthrospira platensis* strain (ZJWST-S1) in the effluent of coupling device, single CEM system, single Fe-C system and two controls (original wastewater and Zarrouk medium) showed that only the wastewater treated by the coupling device was suitable for cultivating *Arthrospira* and the related growth rate of ZJWST-S1 (0.172 g/L/d) was similar to that in Zarrouk medium (0.194 g/L/d). This work presented an alternative pretreatment method of wastewater with high ammonium content and dark colour for *Arthrospira* cultivation, which not only eliminated the inhibitions but also retained the useful nutrients (nitrate and nitrite) for *Arthrospira* growth.

Keywords: Iron-carbon micro-electrolysis; Cation exchange membrane; Colour; ammonium; *Arthrospira*

1. Introduction

With the rapid development of piggery industry and widespread application of anaerobic digestion in China, increasing quantities of digested piggery wastewater (DPW) are being discharged. DPW can contain up to several hundred mg ammonium and thousand mg COD/L, which are

much higher than municipal sewage. On the other hand, the ratios of carbon/nitrogen (C/N) and BOD_5/COD (B/C) of DPW are much lower than municipal sewage [1,2]. Conventional biological treatment processes, such as anaerobic/oxic (A/O) process and anaerobic/anoxic/oxic (A2O) process, are increasingly adopted by many researchers and engineers, as aforementioned processes are economical and mature [3,4]. However, the nitrogen (ammonium and nitrite) and COD are hard to remove in meeting related discharge standards, especially without external carbon addi-

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tion [5]. Consequently, high concentrations of nitrogen and phosphorus remained in the biologically-treated effluent would result in severe eutrophication in rivers and lakes. Furthermore, the heavy metals (such as zinc and copper), colour, etc. will also cause environmental problems. Obviously, a single technology or process like biological treatment is difficult to solve the DPW problem in an effective and low-cost way.

Microalgae-based wastewater treatment method has been increasingly investigated since Oswald put forward it in 1957 due to its advantages in contaminant removal and high-value biomass harvest [6,7]. The residual contaminants (nitrogen, phosphorus, micro element, etc.) in the biologically-treated effluent are also abundant and essential nutrients for microalgae cultivation. However, the high ammonium concentration in the effluent can be toxic to many algae, including *Arthrospira* [8,9]. Therefore, dilution of the effluent before being used as *Arthrospira* cultivation medium is usually one of the most common choices for many researchers. Large volumes of pure water, as a result, are required which are unsustainable in large-scale systems [10]. On the other hand, the colour of DPW effluent usually not tends to decrease but increase after exposing excess aeration in biologically-treated process. This situation will cause light limitation for *Arthrospira* growth, therefore inhibiting its growth as well as the rate of nutrient recovery from the wastewater [10,11]. Thus, further treatment of biological system effluent aiming at removing ammonium, colour, etc. is crucial to *Arthrospira* cultivation.

Iron-carbon micro-electrolysis (Fe-C) is widely used as a low-cost treatment method for acid wastewater to improve biodegradability and remove colour [12–14]. Numerous microscopic galvanic cells are naturally formed between iron and carbon when Fe-C particles are in contact with wastewater. Fe^{2+} , hydroxyl and nascent hydrogen released from the galvanic corrosion reaction are highly active in the reduction of nitrite/colour and the decomposition of refractory organic pollutants, which might decrease the inhibitors to the growth of *Arthrospira* [15,16]. However, the outstanding performance of Fe-C micro-electrolysis almost only occurs under acidic conditions [17], while the biological system effluent is usually alkaline. In other words, the effect of Fe-C micro-electrolysis cannot be durable in such alkaline wastewater. On the other hand, a portion of nitrite and nitrate might be reduced into ammonium form after micro-electrolysis, which will build up toxicity for *Arthrospira*. Therefore, keeping the acidity of the system constant and removing ammonium continuously from it are of great importance to provide Fe-C an ideal reaction condition as well as a suitable culture medium for *Arthrospira*.

In this research, it could be interesting to combine Fe-C micro-electrolysis with cation exchange process, for it could simultaneously provide H^+ and remove NH_4^+ through cation exchange membrane. Therefore, colour, parts of refractory organic pollutants and ammonium in DPW could be enduringly removed in the iron-carbon micro-electrolysis and cation exchange membrane coupling device (Fe-C & CEM). Based on above mentioned viewpoints the enhancement of *Arthrospira* productivity in the wastewater treated by Fe-C&CEM was investigated.

2. Materials and methods

2.1. Piggery wastewater used in experiments

The wastewater used in this study was the DPW treated by intermittent aeration sequencing batch reactor (IASBR) which could achieve stable nitrification and thereby save 25% of the aeration energy and 40% of the external carbon source [18]. The IASBR effective volume of 10 L ($\Phi 25 \text{ cm} \times \text{H}30 \text{ cm}$) were operated at a cycle duration of 8 h. In each cycle, wastewater was fed within 10 min, then four consecutive 40/60 min non-aeration/aeration phases, and then settled for 60 min before drainage. The liquor was stirring mixed with a paddle at a speed of 100–200 r/min during the non-aeration period. The dissolved oxygen (DO) concentration was controlled at 0.5–1.5 mg/L by adjusting air flow rate with an air flow meter during the first aeration phase. Water temperature was 25°C–30°C. The mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) concentration of the system were 5.5 g/L and 2.8 g/L, respectively. The wastewater had an initial content of NO_3^- -N of 136.2 mg/L, NO_2^- -N of 297.4 mg/L, PO_4^{3-} -P of 19.5 mg/L, ammonium of 221.3 mg/L and colour of 968 mg Pt/L. The more detailed physico-chemical characteristics of the wastewater are shown in Fig. 1. The parameters of the wastewater were analyzed according to the Standard Methods for the Examination of Water and Wastewater, 21st ed [19].

2.2. Iron-carbon micro-electrolysis and cation exchange membrane coupling device

The experimental equipment with an effective volume of 1.6 L was separated into two equal size chambers with a piece of polyethylene heterogeneous cation exchange membrane (GrION Environment) (Fig. 2). One chamber was filled with approximately 250 mL wastewater and 300 mL iron-carbon composite material (Fe-C, calcined at 1200°C under nitrogen with an iron/carbon ratio of 1.5 and particle size 3–5 mm) that had been pre-impregnated in wastewater for 48 h, and another chamber was filled with 450 mL sulfuric acid (10 w%). The cation exchange process

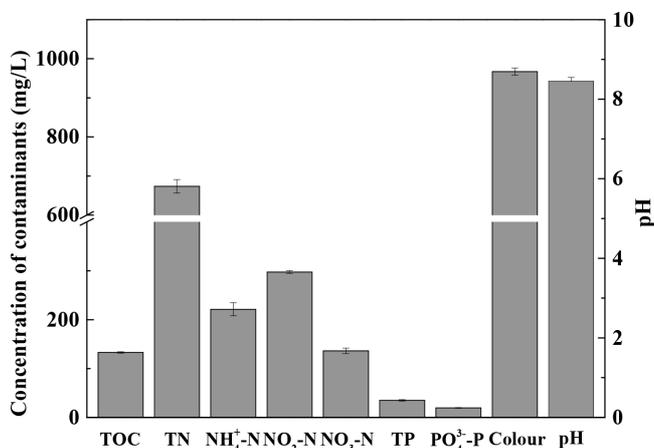


Fig. 1. Physico-chemical characteristics of the wastewater.

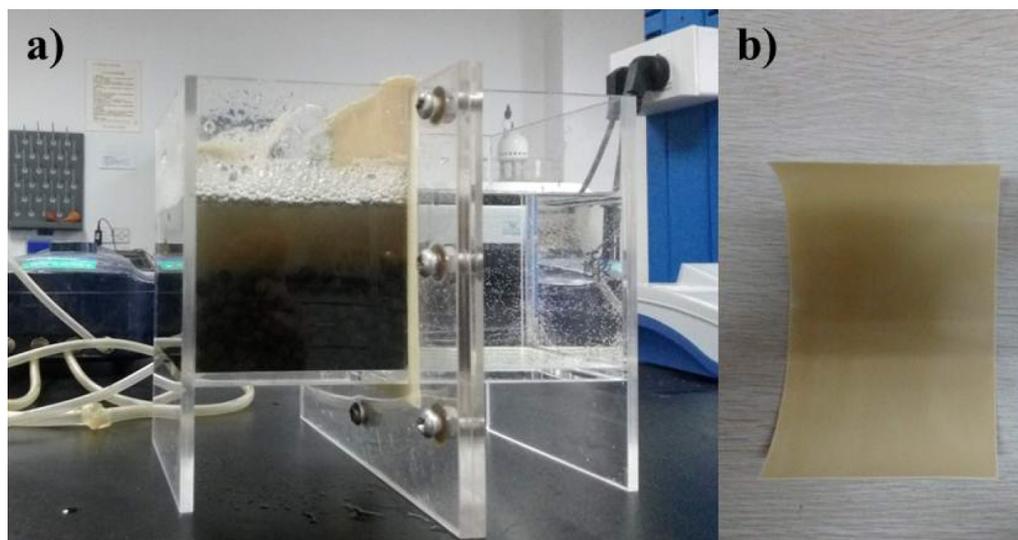


Fig. 2 (a) photograph of two-chamber Fe-C&CEM coupling device and (b) CEM.

and micro-electrolysis reaction were simultaneously operated for 2 h with aeration in our own lab with a constant temperature of 20°C. Then the pH of the wastewater was adjusted to 8.5 by adding 5 M NaOH which could precipitate the ferrous ion from the aqueous wastewater and provide a suitable alkaline environment for *Arthrospira* growth.

2.3 Cultivation of *Arthrospira*

The *Arthrospira platensis* strain (ZJWST-S1) used in this study was isolated from a digested piggery wastewater (DPW) storage pool in Jiaying City, China and possessed a high growth rate in DPW that had been demonstrated in our previous studies [9]. Cultivation experiments of ZJWST-S1 were carried out in 250 ml erlenmeyer flasks which had been pre-filled with 100 ml Zarrouk medium [20] or treated wastewater with 16.8 g/L NaHCO₃ added. It is noteworthy that nitrate is the single nitrogen source in 'Zarrouk medium' with the NO₃⁻-N concentration of 411.8 mg/L. *Arthrospira* strains in logarithmic growth phase were inoculated into the flasks, achieving a final algae density of 0.3 in terms of OD₅₆₀. OD₅₆₀ is the optical density measurement at a wavelength of 560 nm using a spectrophotometer, which could indicate dry cell mass concentration of *A. platensis*. The flasks were then sealed with aluminum film and cultivated in an illuminating incubator (GZP-450, Jinghong Laboratory Instrument Co. Ltd, Shanghai, China) for 10 days. The culturing temperature was maintained at 30 ± 1°C. The light for *Arthrospira* cultivation in this study was provided by fluorescent lamps (white type) on the four sides of the illuminating incubator. The photo period was 12 h light (6000 ± 2000 lux) and 12 h dark. The biomass was calculated according to its relationship with OD₅₆₀, as follows: $y = 0.7178x + 0.0025$ ($R^2 > 0.997$), where y (g/L) is the dry cell weight; x is the absorbance at 560 nm. OD₅₆₀ of the mixed liquor in the flasks was measured after shaking by hand once per day. All of the above cultivation experiments were conducted in triplicates.

2.4 Analytical methods

FTIR spectra were obtained on a Nicolet Avatar 660 using the KBr pellet method. Fe-C and precipitation morphology and surface composition were investigated using a scanning electron microscope (SEM) with Energy Dispersion X-ray Spectrometry (EDX) capability (ZEISS SIGMA, Germany). Inorganic ions (Na⁺, K⁺, Mg²⁺, Ca²⁺) in wastewater were analyzed by cation chromatography (DIONEX ICS-90, USA). The data were analyzed using the Origin 9.0 program (OriginLab, Northampton, MA, USA) according to the methods provided by the manufacturer of the test kit.

3. Results and discussion

3.1 Simultaneous removal of ammonium, colour and TOC by coupling device

The wastewater treatment efficiency of the coupling device was compared with the single CEM system and the single Fe-C system, respectively, as shown in Fig. 3.

The nitrogen, colour and TOC were reduced to different degrees after being treated by the three devices. As for the single membrane system, although it removed ammonium from 231 mg/L to 78 mg/L with a removal rate of 66.2 % which was nearly as high as the coupling device (77.5 %) (Fig. 3a), it had slight effect on colour removal (Fig. 3b). Unexpectedly, the nitrite in the wastewater decreased significantly, which might be the combined effects of aeration, cation exchange membrane and the decreasing wastewater pH with the cation exchange process. In the single Fe-C system, due to the alkalinity of the wastewater and aeration of the operating condition, the half-cell reaction of carbon cathode can be represented as $O_2(g) + 2H_2O + 4e^- \rightarrow 4OH^-(aq)$, $E^0(O_2/OH^-) = +0.40$ V [21]. The generated OH⁻ increased the effluent pH which would gradually passivate the iron-carbon composite material by forming an oxidation layer on its surface. As a result, only a small part of colour, nitrogen and TOC were removed by single Fe-C sys-

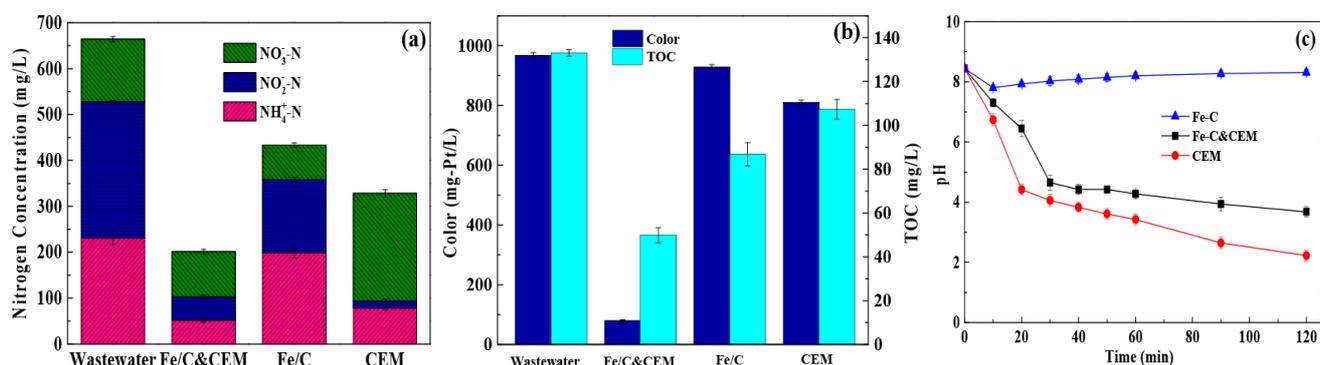


Fig. 3. Wastewater treatment efficiency of the coupling device (Fe-C&CEM), single CEM system (CEM) and single Fe-C system (Fe-C): **a** the concentration of inorganic nitrogen in wastewater after being treated by the three devices, **b** the concentration of colour and TOC in wastewater after being treated by the three devices, **c** the wastewater pH value in the three devices during the 2 h treatment. (Experiment condition: temperature = 20°C, operation time = 2 h, dosage = 1.2 g/mL).

tem with a slight pH increase of wastewater. In particular, among nitrogen, nitrite was removed the most followed by nitrate and ammonium. It was because the removal of contaminant by Fe-C was mainly through reduction effect, and nitrite was more easily reduced when compare with nitrate and ammonium [22,23]. In addition, it was notable that the nitrite and nitrate might not transform into ammonium but nitrogen. Because the concentration of ammonium, as shown in Fig. 3a, did not increase after the reduction of nitrate, but decreased from 221.3 mg/L to 190.9 mg/L. This was mainly attributed to ammonium adsorption by iron and/or activated carbon [24]. As expected, the coupling device combines the advantage of Fe-C and CEM and performs better than either of the single systems at colour, nitrite, TOC removal or ammonium decrease. In Fe-C&CEM, 83% of nitrite and 77% of ammonium were removed respectively, and the remained concentrations were below the corresponding toxic limits to *Arthrospira* [9]. Furthermore, the remained nitrite concentration in Fe-C&CEM was higher than that in single CEM system, which might do better in promoting the growth of *Arthrospira* [25]. Nitrate, the safest nitrogen source for *Arthrospira*, was retained approximately 72%. Meanwhile, the colour was dramatically decreased from 961 to 79 mg-Pt/L which would significantly reduce the light limitation.

On the one hand, the ammonium in wastewater was exchanged with H⁺ through CEM which not only decreased the ammonium but also introduced H⁺ and produced an acidic environment for Fe-C. The cation chromatography results showed that Na⁺ (201.2 mg/L), K⁺ (187.8 mg/L), Ca²⁺ (168.9 mg/L) and Mg²⁺ (21.1 mg/L) were the main cations in the wastewater except NH₄⁺, and with the corresponded residual concentration of 69.1 mg/L, 54.2 mg/L, 73.8 mg/L and 8.5 mg/L after Fe-C&CEM treatment (without pH adjustment by NaOH solution), respectively. These cations were impossible removed by precipitation or other forms in such an acid environment, except for cation exchange as the NH₄⁺ did. As a result, these cations in wastewater were also exchanged with H⁺ in sulfuric acid (10 w%) through CEM which introduced H⁺ and produced an acidic environment for Fe-C as well. Thus, the half-cell reaction of carbon cathode was changed to follow as O₂(g) + 4H⁺(aq) + 4e⁻ → 2H₂O, E⁰ (O₂/H₂O) = +1.23 V [21]. Obviously, its potential difference was much higher than that in alkaline condition,

which also indicated that the reaction of micro-electrolysis was accelerated. As a consequence, more nitrite, colour and TOC were removed by the coupling device when compared with the single Fe-C system under the same reaction time. Additionally, the consumption of H⁺ in wastewater by Fe-C in the coupling device caused the rise of pH compared with single CEM system (Fig. 3c). It enlarged the chemical potential of the cation exchange and also promoted the process that resulted in a better ammonium removal performance of coupling device than that of single CEM system.

SEM images and EDX of Fe-C before/after reaction and the precipitation were obtained (Fig. 4). Obviously, the Fe and C were the main elements of Fe-C before/after reaction, even though the proportion of Fe element was decreased after reaction. Meanwhile, it was noteworthy that the P element was only detected in the precipitation, which also indicated the phosphorus in the wastewater might be removed by precipitation.

In addition, FT-IR analysis (Fig. 5) of the Fe-C before/after reaction and the precipitation were conducted. The peak at 1040 cm⁻¹ that appeared on the precipitation showed characteristic stretching frequencies of P–O vibration [26]. Thus, it could be confirmed that the phosphate in the wastewater was removed by precipitation rather than adsorption on Fe-C.

The probable mechanism of high efficiency of contaminants removal in the coupling device is illustrated in Fig. 6. The high concentration of ammonium and other lower concentrations of cations in the wastewater were rapidly exchanged with H⁺ through CEM, which not only decreased the ammonium concentration but also the pH of the wastewater. Then the reaction of micro-electrolysis was accelerated, and more nitrite, colour and TOC were removed by Fe-C micro-electrolysis process in an acidic environment. At last, the phosphate in the wastewater was removed by precipitation rather than adsorption on Fe-C.

3.2. Cultivation of *Arthrospira* with the coupling device effluent

In order to evaluate the influence of coupling device treatment on enhancing wastewater quality for *Arthrospira* cultivation, ZJWST-S1 was cultured with the coupling device effluent and four controls (raw wastewater, single

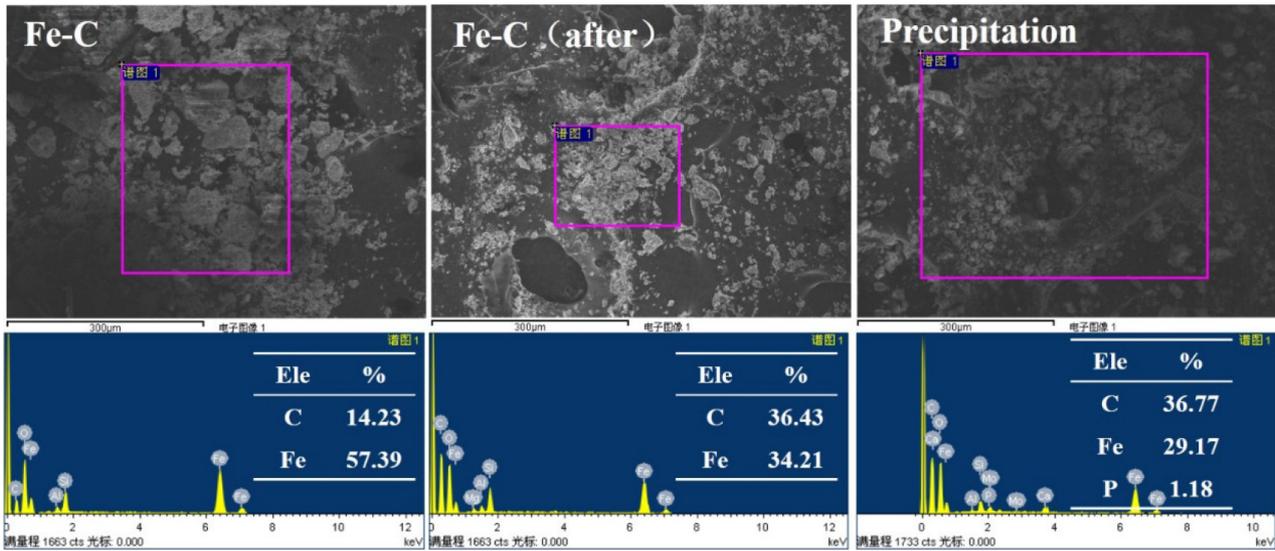


Fig. 4. SEM images and EDX spectra analyses of Fe-C before/after reaction and the precipitation.

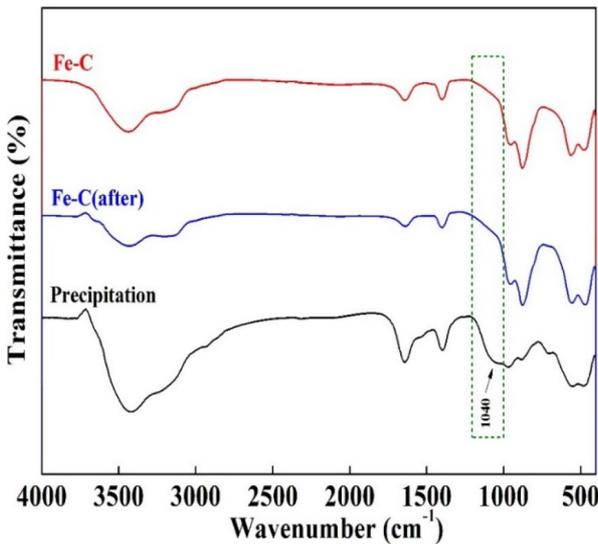


Fig. 5. FT-IR spectra of Fe-C before/after reaction and the precipitation.

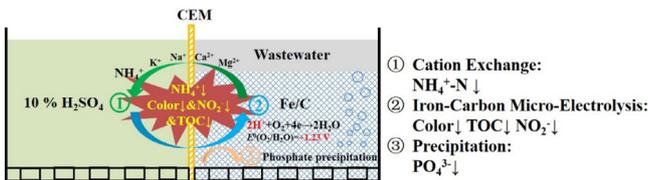


Fig. 6. Schematic diagram of the mutual promoted effects on cation exchange and Fe-C micro-electrolysis in the coupling device.

Fe-C treated wastewater, single CEM treated wastewater and Zarrouk medium), respectively, and the results of batch experiments are shown in Fig. 7.

The coupling device effluent and single Fe-C treated wastewater were both added approximate 20 mg/L $\text{PO}_4^{3-}\text{-P}$

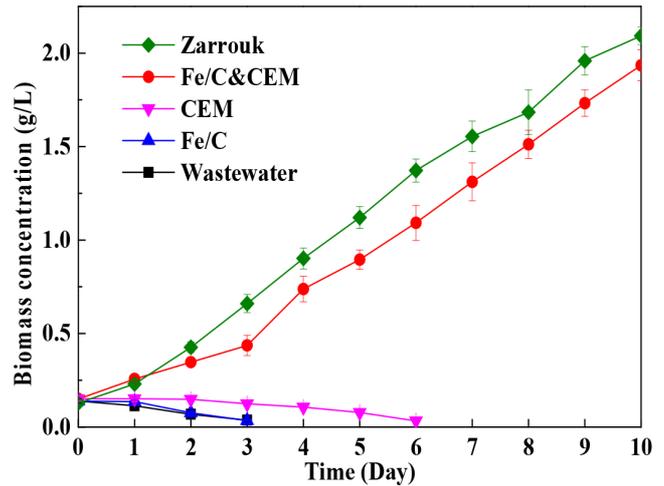


Fig. 7. Growth rate of *A. platensis* ZJWST-S1 in the three device effluent and the controls (raw wastewater and Zarrouk medium), (Experiment condition: Temperature = $30 \pm 1^\circ\text{C}$, Light intensity = 6000 ± 2000 lux, Day–night cycle = 14–10 h).

and in keeping with raw wastewater, because the original phosphate in wastewater was almost removed in the precipitation process. Meanwhile, there was nearly no phosphorus loss for the single CEM treated wastewater, therefore no extra phosphate was added.

The growth rate of ZJWST-S1 in coupling device effluent (0.172 g/L/d) was similar to that in Zarrouk medium (0.194 g/L/d). It was noteworthy that Zarrouk medium as a common medium for *Arthrospira* cultivation, whose cost was much more expensive than Pig Wastewater [27]. Thus, the wastewater treated by the iron-carbon micro-electrolysis and cation exchange membrane coupling device had advantage in cost efficiency for cultivating *Arthrospira*. On the other hand, although the nitrite and colour were able to be removed by single Fe-C micro-electrolysis, ZJWST-S1 cannot grow in the related effluents. This was because the

ammonium in Fe-C effluent still reached up to 200 mg/L that was too high and toxic for *Arthrospira* growth [28]. On the contrary, the single CEM process could remove only partial ammonium and little colour through cation exchange, thus the still high ammonium concentration and dark colour inhibited the growth rate of *Arthrospira*. Correspondingly, the *Arthrospira* also cannot survive in that medium and die in 6 days. As to the raw wastewater, its ammonium, nitrite and colour were all inadaptable for *Arthrospira* growth, obviously, ZJWST-S1 died in 3 d (Fig. 7).

4. Conclusion

A novel wastewater treatment coupling device which integrates the advantages of Fe-C micro-electrolysis and cation exchange membrane has been successfully designed and operated for *Arthrospira* cultivation. In the coupling device, 77% of ammonium and 92% of colour were removed respectively and below the corresponding toxic limitations, which are the two main inhibiting factors for *Arthrospira* cultivation. More importantly, the cation exchange process and Fe-C micro-electrolysis process are mutually promoted, and obtained better treatment efficiency than single system on ammonium, colour and TOC. Meanwhile, the nitrite and nitrate were retained to appropriate concentrations. Hence, the cultivation of *A. platensis* ZJWST-S1 in the three device effluents and controls showed that only the wastewater treated by the coupling device was more suitable for cultivating *Arthrospira* and the related growth rate of ZJWST-S1 (0.172 g/L/d) was similar to that in Zarrouk medium (0.194 g/L/d).

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