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A comparative study of the anaerobic baffled reactor and an integrated anaerobic baffled reactor and microbial electrolysis cell for treatment of petrochemical wastewater

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HIGHLIGHTS

- The performance of ABR-MEC were affected by the applied voltage and the HRT.
- The applied voltage on electrode improved the performance of the ABR-MEC reactor.
- Decreasing of HRT leads to the decreased removal rate of COD and methane production.
- Energy consumption could be neglected compared to the incremental methane at 1 V.
- The increase of voltage and higher HRT leads to improving stabilization of ABR-MEC.

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ABSTRACT

The aim of this study was to evaluate and compare the treatment of petrochemical wastewater with an integrated anaerobic baffled reactor and microbial electrolysis cell (ABR-MEC) and anaerobic baffled reactor (ABR). For this purpose, the effect of hydraulic retention time (HRT) and applied voltage on the performance of ABR-MEC reactor were investigated in four phases. Regarding the results, the maximum COD removal efficiency in the ABR-MEC reactor was higher than that in ABR reactor, i.e. 96.5% versus 66.7%. Also, the maximum of yield CH_4 in ABR-MEC reactor was 1.4-fold than ABR reactor. The results show that the applied voltages can increase the removal of chemical oxygen demand, methane production, accelerate the conversion of volatile fatty acids and maintain the appropriate pH range for methanogen growth.

1. Introduction

The petrochemical industry, including petrochemical processing, natural gas production, and oil refining, produces large amounts of wastewater. The wastewater originating from the petrochemical industry contains organic and inorganic compounds, including oil, aliphatic and polycyclic aromatic hydrocarbons, metals, salt, sulfide, cyanide, octanol, formaldehyde, volatile phenol, and other chemicals, usually used in the petrochemical industry [1–3]. Different pre-treatment and treatment methods are employed to treat petrochemical wastewater. These methods are inclusive, biological, and physical-chemical methods. The conventional treatment of effluents in petrochemical wastewater is based on the mechanical and physicochemical methods such as coagulation and oil-water separation. However, these processes are subject to several restrictions, such as high operational and investment costs. Furthermore, physical treatment has many disadvantages such as low effectiveness. On the other hand, the biological treatment method has a number of advantages, including simple management and low operational and investment costs. There are two types of biological treatment methods, aerobic and anaerobic. The anaerobic

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treatment has several advantages compared to the aerobic treatment, such as lower capital and operating costs, less energy requirement, lower sludge production, simpler design and operation, and the conversion of organic matter to biogas and bioenergy [4–6]. However, anaerobic treatment reactors suffer from several disadvantages such as their requirement for a longer start-up period of time to develop the microbial community as well as sensitivity to temperature changes [6].

The anaerobic baffled reactor (ABR) was developed by Bachmann and McCarty. This reactor has numerous advantages, such as simple design, long biomass retention time, low production of sludge, and separation of both acidogenesis and methanogenesis [7–9]. However, the ABR faces several disadvantages, including accumulation of volatile fatty acids, being sensitive to toxic compounds, low methane content in biogas production [10]. Therefore, to improve the performance of the ABR in the treatment of petrochemical wastewater, this technology requires auxiliary processes to increase the treatment efficiency. Compared with conventional anaerobic treatment, it has been shown that a Bioelectrochemical system (BES) could effectively increase the reductive rate of toxic pollutants and methane production. The BES is a new approach to stimulate the anaerobic degradation of hydrocarbons [11]. There are two types of BES with regard to the way of using electricity. Microbial fuel cell (MFC) generates electricity from organic materials, while microbial electrolysis cell (MEC) need electricity supply for generating bioenergy from organic materials.

In the MEC, the organic substrate is electrochemically oxidized by active bacteria, leading to the production of protons and electrons in the anode [12]. The electrons are transferred to the anode surface by exoelectrogenic bacteria and the protons are released into solution. Eventually, electrons travel through the external circuit to a cathode [13]. Previous studies have demonstrated the MEC is a microbial electrochemical technology using bioelectrochemical reactions to upgrade biogas production in an anaerobic digestion (AD) through the rapid degradation of highly concentrated organic wastewater, volatile fatty acids)VFAs(, toxic materials, resistant compounds, and non-degradable organic substrates [14]. The VFAs are generated in the anaerobic reactors; however, this intermediate product could not be mainly converted to methane. Based on the Nernst equation, an extra energy input is needed to convert VFAs to biogas. According to recent studies, the VFAs can be converted into hydrogen by applying voltage [9,15]. Moreover, several studies declared that an AD coupled with a microbial electrolysis cell would lead to an improvement in the generation and purity of biogas simultaneously [16]. These results indicated that bioelectrochemical reactions enhanced the methane production by the motivation of microbial activities and the increase of the removal of organic matters, including VFAs [14]. Generally, previous studies declared that the applied voltages could increase the removal in the chemical oxygen demand, accelerate the conversion of volatile fatty acids, upgrade the methane content, increase methane production, and maintain an optimal pH level for methanogen growth [13].

However, no studies have yet examined the treatment and methane production from petrochemical wastewater using ABR and ABR-MEC reactors to verify the effectiveness of MEC. Hence, the aim of this study was to evaluate and compare the treatment of petrochemical wastewater with an integrated anaerobic baffled reactor and microbial electrolysis cell and anaerobic baffled reactor. For this purpose, in phase I, the ABR-MEC reactor was started without applied voltage at HRT of 72 h. In phases II– IV, the petrochemical wastewater was continuously fed into the ABR-MEC at HRTs of 72, 60, and 48 h, respectively and the effect of the applied voltage at 0.6, 0.8, and 1 V on reactor performance was investigated in terms of chemical oxygen demand (COD), methane production rate, the content of methane, VFAs concentration, and the stability of reactor.

Table 1
Physicochemical characteristics of petrochemical wastewater.

Parameter	Concentration (mg/l)
COD	1820–2200
BOD	600–870
pH	8.1–8.3
Conductivity (ms/m)	1–1.2
Total phosphorus (mg/L)	1–2
Total nitrogen (mg/L)	5–11

2. Materials and methods

2.1. The petrochemical wastewater characteristics

The petrochemical wastewater used in this study was collected from a petrochemical industry located in Isfahan (Iran). The petrochemical wastewater was stored in a cooled room at 4 °C and brought to room temperature before feeding to the reactors. The physicochemical characteristics of wastewater used in this study is shown in Table 1.

2.2. The configuration of the ABR-MEC and ABR reactor

The laboratory-scale ABR-MEC and ABR reactor were made of perspex and include four sequential compartments (sequentially named C1– C4). The reactors were 32 cm long, 8 cm wide and 10 cm deep with a total volume of 2.5 L. The reactors in this work have 0.5 L headspaces and 2 L working volume. Each of the 4 identical compartments included an up-flow region and a down-flow region with a volume ratio of 4:1. The up-flow zone was equipped with 4 equidistant sampling ports (Fig. 1). The anodes and cathodes were fixed in the up-flow region of each last two compartments and each one connected with external power supply through titanium wire. The temperature of reactors was controlled by a water jacket to maintain the operation at a constant mesophilic temperature of 34 ± 1 ℃

Before the start-up of the ABR-MEC, the exoelectrogens on the anodes were inoculated in microbial electrolysis cells fed with glucose medium for three months. Also, the ABR reactor was operated as a control reactor without internal electrodes. The inoculum was obtained from an anaerobic digester at a wastewater treatment plant in Isfahan (Isfahan, Iran). The ABR-MEC and ABR reactors were inoculated with the anaerobic sludge with a mixed liquor suspended solids (MLSS) content of 25,740 mg/l and mixed liquor volatile suspended solids (MLVSS) 11,100 mg/l. The anodes (7 × 6 cm) were made of carbon cloth and cathodes 7 × 6 cm) were made of stainless-steel mesh (ss316). The electrodes were placed in last two compartments. The distance between the anode and cathode was 2 cm. The electrical current through the system was monitored and recorded by a data logger (ELR2510, Iran) connected to the electrodes. The influent was pumped continually with a peristaltic pump (PRP-TN-556, TOOS NANO Company, Iran) into the ABR-MEC and ABR reactors. Biogas was collected in gas bags which were attached on the top of the ABR-MEC and ABR reactors. The alkalinity of the influent was kept at 2000 mg-CaCO3/l.

2.3. Analytical methods and calculations

Chemical oxygen demand and alkalinity were measured using standard methods [17]. The pH was measured using a pH meter (model 744). The TVFAs was determined according to methods previously described [18]. The biogas was analyzed by a gas chromatography (Sp-3420 A, Beijing Beifen Ruili Analytical Instrument CO) equipped with a packed column (Porapack Q, Chrompack, 3 m length, 3 mm ID, stainless steel, Germany) with a thermal conductivity detector and the injection temperature of 140 °C. Nitrogen was used as the carrier gas with a flow rate of 20 ml min^{-1}. Gas samples were injected with a 250 μL pressure

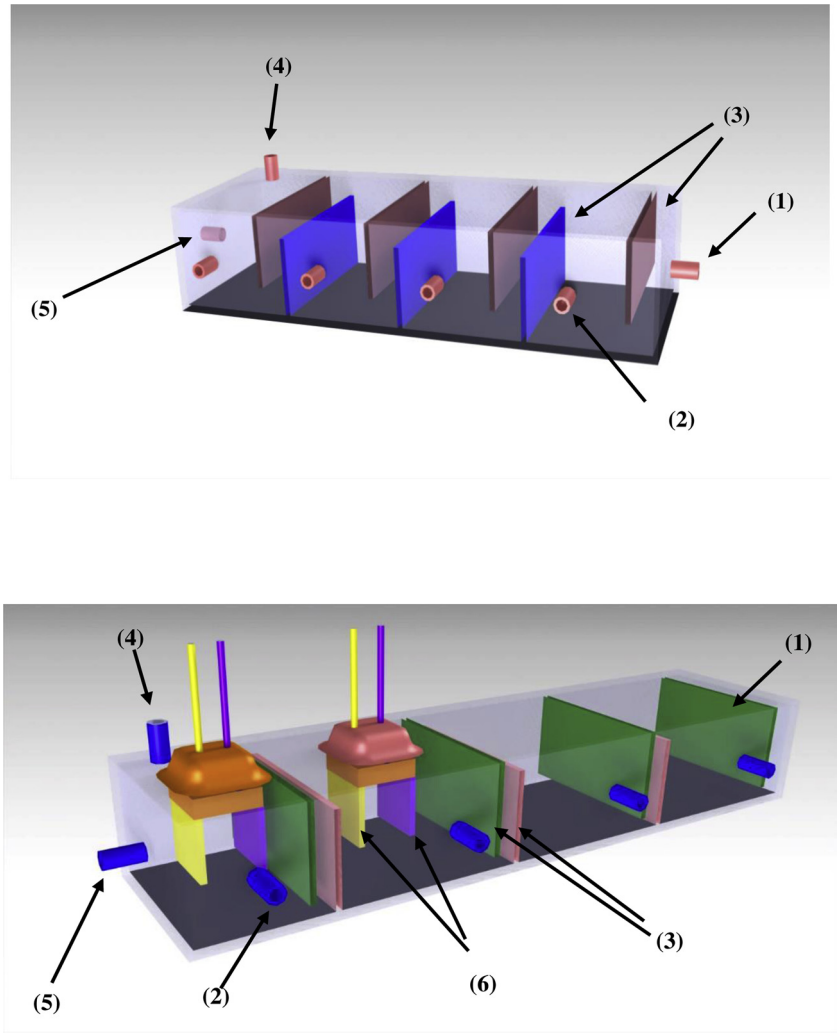

Fig. 1. Schematic diagram of the ABR-MEC and ABR reactor.

lock gas syringe (SGE, Australia). The biogas production was measured by liquid displacement method. Volatile fatty acids were measured using a gas chromatography (Sp-3420 A, Beijing Beifen Ruili Analytical Instrument CO) equipped with a flame ionization detector and PB-21 capillary ftemperature was adjusted between 45 °C and 125 °C (4 min at 45 °C and then 25 °C/min to 125 °C) and the temperatures of injector and detector were adjusted to be 115 and 200 °C, respectively.

Partial alkalinity (PA, titration from the original pH sample to pH 5.75, an alkalinity which corresponds roughly to bicarbonate alkalinity) and total alkalinity (titration to pH 4.3) were determined to obtain intermediate alkalinity (IA, titration from 5.75 to 4.3, approximately the VFA alkalinity). The IA:TA ratio was used as a tool to monitor anaerobic digestion, considering that the process was stable when the IA: TA was below 0.3 [19].

The Coulombic efficiency (C_E %) was calculated on the basis of measured coulombs of current compared to the total coulombs from substrate removed (based on COD) as presented in equation (1):

$$C_E = \frac{8I}{FqΔCOD} \tag{1}$$

where I is the current (A), F is Faraday's constant, q is the volumetric influent flow rate (l/s), and $ΔCOD$ is the difference between the influent and effluent COD (g/l) [20].

Electric energy supply (W_E) in ABR-MEC reactor was calculated according to the following Eq. (2):

$$W_E = \sum_{1}^{n} IE_{ap}Δt \tag{2}$$

where I is the current (A), E_{ap} is the applied voltage, $Δt$ is the time of the experiments [21].

Energy income in ABR-MEC reactor from the increased methane production (W_{CH_4}) was calculated based on our previous study as follow:

$$W_{CH_4} = \frac{ΔtΔH_{methane}(V_1 - V_2)}{V_m} \tag{3}$$

where $ΔH_{methane}$ is the energy content of CH_4 based on the heat of combustion (upper heating value) (891 kJ/mol), $Δt$ is the time of experiments (hour). V_1 is the accumulative CH_4 production in the ABR-MEC reactor (ml/h), V_2 the accumulative CH_4 production in the control reactor (ml/h) and V_m is molar volume of the gas.

Energy efficiency (η_E) relative to the electric energy supply and energy output was calculated by the following Eq. (4):

$$\eta_E = \frac{W_{CH_4}}{W_E} \times 100 \tag{4}$$

2.4. Start-up and operation of ABR-MEC reactor

In this study, the COD value of the influent petrochemical wastewater varied from 1820 to 2200 mg/l. First, ABR and ABR-MEC reactor

started up to reach steady state condition. Then ABR reactor operated in three phases. In phase I, the ABR reactor was operated in a continuous mode at HRT of 72 h. In phases II, III, the ABR reactor was operated at HRT of 60 and 48 h, respectively. Also, in phase I, the ABR-MEC reactor was started with petrochemical wastewater without applied voltage at HRT of 72 h for 3 weeks (as an anaerobic treatment). At this phase, the ABR-MEC reactor was operated in continues mode without applied voltage, so as to stabilize the biofilm on the electrodes. In phase I, the ABR-MEC was as an ABR reactor contains two pairs of electrodes. In this phase, the role of composed biofilm on the electrode was evaluated in the performance of the ABR-MEC reactor. After the reactor reached to steady state condition, the operation phases were started. In next three phases, the effect of applied voltage was investigated on reactor performance as COD removal, VFAs and methane production, and current intensity, at 0.6, 0.8 and 1 V. In phases II–IV, the ABR-MEC reactor was operated at HRT of 72, 60 and 48 h, respectively. For ABR-MEC reactor, the experimental period was divided into four phases, as are provided in the supplementary material. Also, the applied voltage in reactor was gradually increased in these phases from 0.6 up to 1 V. After the stability of reactor in each phase, the applied voltage was changed. The steady state condition is achieved when the changing rate of parameters such as COD is impalpable [8].

3. Results and discussion

The ABR-MEC reactor performance was described by using several main parameters, electricity generation, VFAs and gas production, and COD removal, alkalinity and pH levels. Summary of achieved results are provided in the Supplementary material.

3.1. Effect of applied voltage and HRT on COD removal

For ABR-MEC reactor, the applied voltage was controlled at 0 V in phase I. The removal of COD rate in the ABR-MEC reactor improved during this phase (Fig. 2). In ABR-MEC reactor, the COD concentration of 589 ± 3 mg/l was achieved at the end of the phase I, while the COD value of 655 ± 5 mg/l was achieved for ABR reactor at HRT of 72 h. It results probably due to the retention of biomass on the electrodes [22].

In the next three phases, the applied voltage in the ABR-MEC reactor gradually increased from 0.6 to 1 V at each HRT. In each phase, the effect of applied voltage on the ABR-MEC performance was investigated. As it presented in Fig. 2a since the third week with biofilm growth on the anode, COD removal started to increase which this increment coincided with applied voltage. According to the results, during the phase II in the ABR-MEC reactor, the COD removal efficiency at 0.6 V was 90.6%. Also, a sustainable efficiency of COD removing was 95% and 96.5% at 0.8 and 1 V, respectively. The results show that the microbial metabolism might have been motivated by the electric current. Actually, the electric current could lead to enhance the degradation of the substrate in the integrated reactor.

As shown in Fig. 2a, for phase III, the COD removal in the ABR-MEC reactor decreased as lowering hydraulic retention time from 60 to 48 h at all applied voltages. In this phase, The COD removal increased from 80.6% up to 84%, and then to 86.4%, as increasing of the applied voltage from 0.6 to 8 V to 1 V, respectively. For the ABR reactor, the results of this study showed that by decreasing the HRTs from 72 to 60 h to 48 h, COD removal efficiencies decreased from 66.7% to 58.4% to 53.8%, respectively. An explanation for this trend is the occurrence of the shocked OLR. In the previous study, when the OLR was increased, the ABR performance was disturbed, leading to a decrease in pH level and COD removal, due to the predominance of fast growth acidogenesis over methanogenesis [23–25].

During all phases, the removal rate of COD increased as a result of gradually increasing the applied voltage from 0.6 to 1 V in ABR-MEC reactor. The increased removal rate of COD could be attributed to higher degradation of organic compounds such as VFAs, by combining a bioelectrochemical system [26]. Also, stepwise decreasing of HRT leads to the decreased removal rate of COD. It seems that the trend of decrease of COD removal in the ABR-MEC reactor was due to the volatile fatty acids accumulation, which lead to bacteria inhibition under a short HRT [27,28].

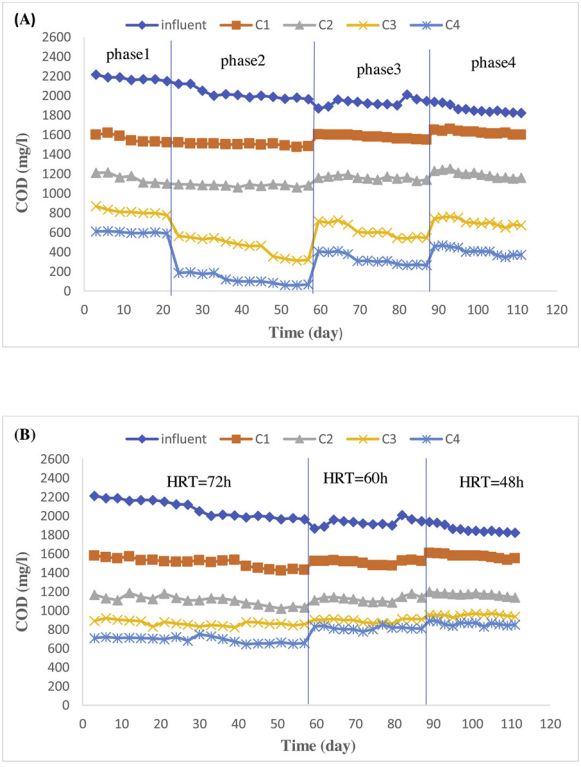

Fig. 2. Performance of the ABR-MEC (A) and ABR (B) reactor in terms of COD removal.

In addition, COD profile changes through the reactor demonstrated that there was not any observable change in each COD phase removal rate of the first and the second compartments in both reactors. However, COD removal rate in the other compartments increased with gradual voltage increment during the second to the fourth phase in ABR-MEC reactor. This evidence showed that applying voltage increases COD removal in ABR-MEC reactor. Also, a reduction in the hydraulic retention time resulted in diminishing COD removal rate in both compartments during the second to fourth phases. This decline in COD removal rate in this later compartment was more than the first one. It seems that it is due to the difference in the microbial community in the compartments. Thus, the front compartment contains fast-growing bacteria which decline in hydraulic retention time had lower effects on its activity, while methanogens which are present in the lower compartments, had a lower growth rate.

In ABR-MEC reactor, The COD removal efficiency was substantially higher than that was obtained by Tong et al., who achieved the COD removal rate of 88% in ABR reactor [29]. Arvin et al. also reported the achievement of COD removal rate of 86% in an anaerobic baffled reactor for treatment of landfill leachate, but it was still lower than that obtained within this research [23]. According to the findings, the removal rate of COD was affected by the applied voltage and the HRT [30].

3.2. Alkalinity level and stability of ABR-MEC reactor

The Alkalinity level is a key parameter that was used to monitor the performance of an anaerobic process [23]. In ABR-MEC reactor, the alkalinity levels of each phase increased as a result of gradually increasing the applied voltage from 0.6 up to 1 V. Also, affected by a

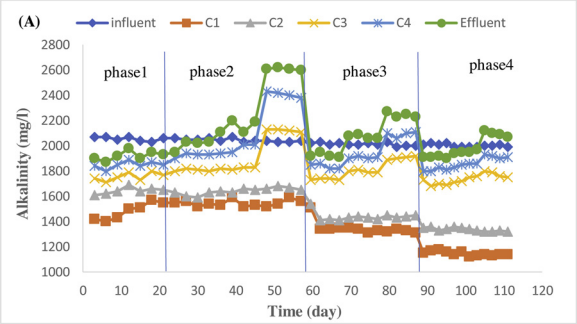

Fig. 3. Performance of the ABR-MEC and ABR reactor in terms of alkalinity level.

reduction of HRT from 72 to 60 h and from 60 to 48 h, alkalinity level decreased, causing accumulation of VFAs. The alkalinity levels, in every four compartments of the ABR-MEC reactor, are shown in Fig. 3a. In all phases, the measure of alkalinity decreased in the former compartments caused by the accumulation of VFAs, while alkalinity levels increased in the latter compartments because of producing CO_3^{-2} and HCO_3^- by methanogens process [26].

In ABR-MEC reactor, the alkalinity levels in the four compartments were 1560 mg-$CaCO_3$/l, 1650 mg-$CaCO_3$/l, 2110 mg mg-$CaCO_3$/l and 2380 mg-$CaCO_3$/l respectively at the end of phase II, while the alkalinity levels in the four compartments of ABR reactor were 1510 mg-$CaCO_3$/l, 1670 mg-$CaCO_3$/l, 1790 mg-$CaCO_3$/l and 1930 mg-$CaCO_3$/l respectively at HRT 72 h. As shown in Fig. 3, the applied voltage in the two last compartments of ABR-MEC reactor increased the alkalinity level in the range of 13–21% than two last compartments of ABR reactor. It seems that the increase of the applied voltage enhances the activity of the microorganisms, leading to a more reduction of VFAs [14]. Investigating alkalinity profile changes through ABR-MEC reactor showed that during each phase there were not any major changes in the first two alkalinity compartments, but in the next two compartments alkalinity increased due to applying voltage and gradual voltage increment. In addition, alkalinity levels decreased by reducing the hydraulic retention time.

Stability in effluent COD concentration, current generation, and proportion IA: TA were considered as the indicators for the steady-state conditions [31]. IA: TA ratio was considered as a useful tool to monitor the anaerobic process, considering that the process was stable when IA: TA was below 0.3 [32]. In ABR-MEC reactor, the IA:TA ratio was in the range of 0.27–0.35, 0.12–0.25, 0.19–0.27 and 0.25–0.4 at the end of phase I–IV respectively. While these ratios were in the range of 0.14–0.34, 0.19–0.54, 0.24–0.6 and 0.14–0.21 at the end of phase I–III respectively in control reactor (Fig. 4).

Our findings show that the gradually increasing voltage leads to improving IA: TA ratio. This result could be attributed to the transformation of VFAs to others components through the application of a voltage or to the effect of IA: TA ratio on both acidogenesis and methanogenesis bacteria [5]. Also, the decline of HRT leads to

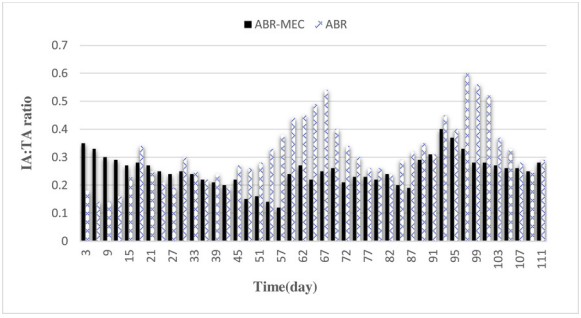

Fig. 4. Stability of ABR-MEC and ABR reactor in the term of IA: TA ratio.

deterioration of IA: TA ratio. It seems that applied voltage rather than hydraulic retention time had an important role in reactor stability. According to the results, the ability to resist shock loading was strengthened in the ABR-MEC reactor in comparison with the control ABR reactor. Our study has demonstrated the applied voltage increase stabilization of an ABR-MEC via bioelectrochemical reactions.

3.3. pH level

The pH level is a key parameter to the evolution performance of the anaerobic process. In anaerobic treatment systems, each microorganism group has different optimum pH values, but the most important microorganisms are methanogenesis. Methanogens are sensitive to changes in pH and the optimal pH range of methanogen activity is 6.8–7.2 [9,33,34]. If pH deviates from the optimized pH range of methanogens, the methanogenic activity decreases. This condition leads to an accumulation of the acetogenesis end products. This parameter was related to alkalinity level and the amount of VFAs. In both reactors, first, pH levels generally decreased due to the fatty acids accumulation by acidogenesis and acetogenesis at former compartments in the reactors. Then, pH level increased due to being consumed by fatty acids at the last compartments [18,27].

In phase I, the pH level was appropriate for growing methanogens in the last compartments of ABR-MEC reactor. During this phase, both parameters were suitable for electrogenic bacteria, growing and overcoming the methanogens in the anaerobic processing reactor. In phases II–IV, pH did not change at two former compartments, while pH increased in the last two compartments as increasing the applied voltage. This result was related to alkalinity level and the amount of VFAs in the reactor. In all phases, the increasing of both pH and alkalinity levels in the last two compartments is due to decreasing the concentration of VFAs [26]. A previous study suggests that the applied voltages in the MEC can improve the enhancement of pH, maintaining pH at a favorable range and therefore improving the growth of methanogens [16]. Also, the decreasing of HRT can lead to a decline in pH in all compartments. The results show that by decreasing the hydraulic residence time, the amount of volatile fatty acids was increased in each of the two reactors compartments. So, the accumulation of volatile fatty acids leads to a decrease in alkalinity and pH levels.

From the data presented in Fig. 5, it can be seen that the pH values in the two first compartments of both reactors were the same. These results can be related to a lack of voltage applied in these compartments but the pH values in the two last compartments of ABR reactor at different HRT were in the range of 6–7.2, while its values in the two last compartments of ABR-MEC reactor at different phases were more stable in the range of 6.7–7.6. According to the results, the pH level was in the range between 4.7 and 5.9 at former compartments of ABR-MEC reactor, which is the optimal pH level of acid-producing bacteria for the successful acidification process. Also, the pH values were in the range between 6.6 and 7.2, which gives an advantageous environment for methanogenic activity in the compartments 3 of the ABR-MEC reactor. Because of the microbial electrolysis of VFAs, the pH level at ABR-MEC

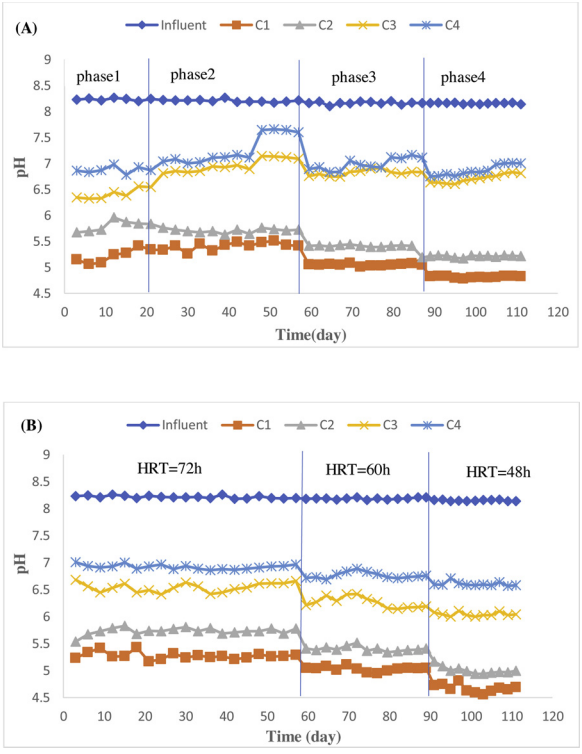

Fig. 5. Performance of the ABR-MEC and ABR reactor in terms of pH.

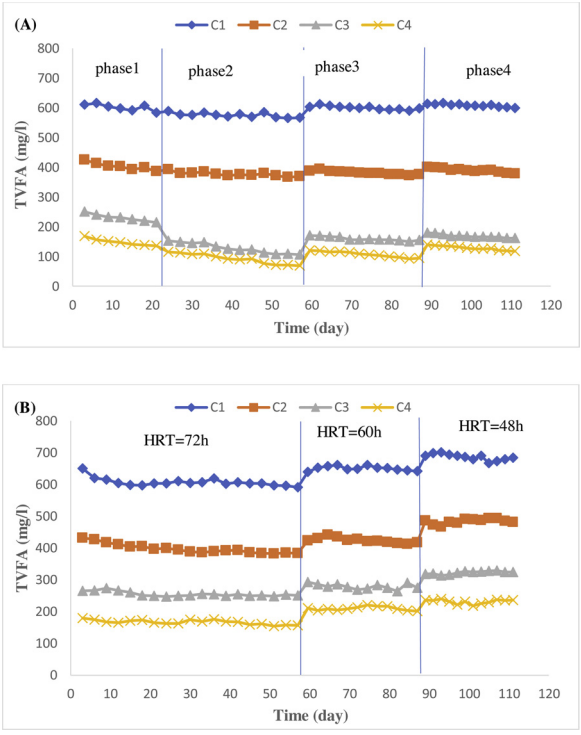

Fig. 6. The profile of total volatile fatty acids (TVFAs), A (ABR-MEC reactor), B (ABR reactor).

was maintained at optimal levels for methanogen growth by applying the voltage [13].

3.4. Effluent VFA concentration

Volatile fatty acids are important intermediate products in the generation of methane, and their concentrations affect the performance of reactors. The VFAs are produced during the acidification process in the former compartments. Then, this intermediate product consumes in the last compartments. However, the VFAs level in the reactor should be less, because of the aggregation of VFAs are in the reactor that leads to the inhibition of methanogens [35]. Although the VFA products in the first compartment and these could be substrates to the following compartments, all of the VFAs could not be further converted into biogas under the limitation of thermodynamics. As a result, an extra energy input should be applied in order to convert VFAs to biogas [9].

In the control reactor, the accumulation of VFAs in the lowest HRT is also reflected in the lowest COD removal (53.8%) as shown in Fig. 6. The VFAs concentration at longest HRT was 156 mg/l, which increased to 201 and 238 mg/l at the HRT 60 h and 48 h. This trend can be confirmed by relatively low COD removal (53.8%) in the control reactor. Previous studies show that the low organic loading rate at the longer HRT leads to low-level concentration of VFAs, while high loading rate increases the accumulation of intermediate products such as VFAs [10].

In ABR-MEC reactor, the concentrations of effluent VFAs were decreased affected by the gradually increasing of applied voltage in ABR-MEC reactor. In phase II, the amount of total volatile fatty acids decreased from 100 to 92 mg/l and from 92 to 69 mg/l as increasing the applied voltage 0.6–0.8 V and 0.8–1.0 V respectively. In phase III, the concentrations of effluent VFAs were higher than that of at phase II. Considering the results, decreasing the hydraulic retention time leads to enhancing the concentrations of VFAs within effluent. This result was matched with decreasing of pH value. Similar results have been reported in other studies [27,36–38]. In phase III, the amount of total volatile fatty acids was decreased from 117 to 103 mg/l and 103 to 94 mg/l as increasing the applied voltage 0.6–0.8 V and 0.8–1.0 V, respectively. In the final phase, decreasing the HRT leads to an enhanced concentration of effluent VFAs. Similar trends have been reported in previous studies. They indicated a significant increase of VFAs with increasing organic loading rates [36,38]. In this phase, the measure of total volatile fatty acids was decreased from 134 to 126 mg/ l and 126 to 118 mg/l as the applied voltage increased from 0.6 to 0.8 V and 0.8 to 1 V, respectively.

Volatile fatty acids concentration changes were also investigated through the reactors. The results revealed that increasing voltage causes an increase in the conversion rate of volatile fatty acids in third and fourth compartments. According to the results, the conversion rate of volatile fatty acids in the third compartment was higher than the fourth one. It seems that the third compartment plays a key role in the volatile fatty acids conversion. As shown in Fig. 3, the concentration of volatile fatty acids in the first compartments was higher than the other compartments, which was significantly reduced due to the consumption of volatile fatty acids in the subsequent compartments (see supplementary material for additional information). The concentrations of effluent VFAs in all phases have been shown in Fig. 6. The results show that a small amount of electric energy reduced VFAs in the effluent reactor by improving the microbial activities [14]. The three main VFAs observed in compartments of ABR-MEC reactor were acetic acid, butyric acid and propionic acid. These intermediate products are consumed as a food source for the subsequent microbial communities. Of these VFAs, acetic acid is considered as the key intermediate product for methane production. In ABR-MEC reactor, the concentration of acetic acid was maximum in the C1 (around 317 mg/l) under applied voltage 1 V at HRT of 72 h. The acetic acid concentration decreased along the ABR-MEC compartments, which was 317 mg/l, 278.3 mg/l, 79.7 mg/l, 70.6 mg/l for C1–C4 respectively (Fig. 7). This decrease in acetic acid concentration indicated that exoelectrogens on the anodes might actively consume acetic acid for the current generation, which was used for the reduction at the cathodes for the methane production.

Based on the results obtained from this study, the ABR reactor could not well the conversion of the intermediate products to methane at

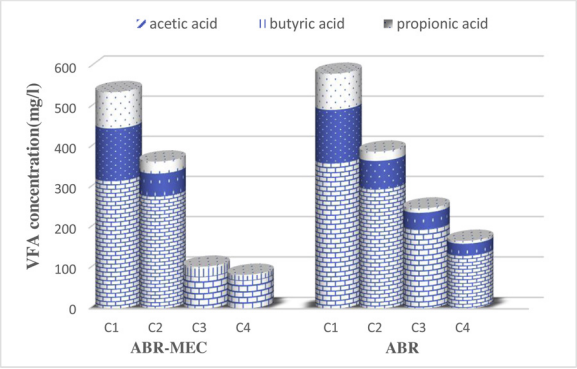

Fig. 7. Variation in dominant volatile fatty acids (VFAs) concentrations across the four compartments of ABR-MEC reactor (C1 to C4) under applied voltage 1 V at HRT of 72 h and variation in dominant volatile fatty acids (VFAs) concentrations across the four compartments of ABR reactor at HRT 72 h.

lower HRT, while the ABR-MEC reactor well consumes the intermediate products to methane at same HRTs. Thus, it can be concluded that there is an equilibrium between acid and methanogenic fermentation in this ABR-MEC reactor compared with ABR reactor.

3.5. Biogas production

At the end of the first phase, the methane production rate in the ABR-MEC reactor was more than this rate in the control reactor. It seems that composed biofilm on the electrode might help to enhance methane production rate in the integrated reactor. In phase II, as applying the voltage at the ABR-MEC reactor, the methane was increased at headspace of the reactor. The production of methane was increased as a result of reducing the concentration of VFA, and conversion of hydrogen ions to methane, via bioelectrochemical reactions [14]. In this phase, the values of hydrogen, methane, and carbon dioxide were accounted as 0.33%, 92.4% and 6.37% within the biogas produced in ABR-MEC reactor at 0.6 V (Fig. 8). By increasing the applied voltage, the proportion of methane and carbon dioxide were altered. Such that, the proportion of methane was increased after each phase. Considering the results, as increasing the applied voltage, along with increasing the COD removal, the proportion of carbon dioxide was decreased, while methane production was increased. The proportion of hydrogen gas did not change by the applied voltage. Bo et al suggested that the increase in applied voltage not only increases the evolution of hydrogen gas, but also increases the activity of hydrogenotrophic methanogens, which played a key role in CO_2 reduction into additional CH_4. So, it appeared that the H_2 could be utilized completely with little accumulation [39].

In phase II, methane production rate was enhanced from 115 ml/day to 127 ml/day and 127 ml/day to 142 ml/day at applied voltages of 0.6 V, 0.8 V, and 1 V respectively.

Also, the proportion of methane and methane production rate was decreased as declining the HRT from 72 to 60 h. The pervious study suggested that the decrease of CH_4 production in the reactor was due to the volatile fatty acids accumulation under a short HRT [34]. The previous studies offered that this effect could be a result of substrate inhibiting at lower HRTs. When HRT is decreased, the methanogenesis tends to alter as acidogenesis during the anaerobic process. So, hydrogen content is increased. Also, the results show that the low and high organic loading rates were suitable for methanogenesis and hydrogen-producing bacteria, respectively [8]. In phase III, the result shows a decline in the methane production, which was due to the consumption of organic compounds such as VFAs. The maximum of CH_4 yield in ABR-MEC reactor was almost 1.1 times higher than that of no voltage added anaerobic process in phase I. Also, this amount was 1.4-fold then the maximum of CH_4 yield in ABR reactor. The biogas production was low and inconsistent in ABR reactor than ABR-MEC reactor during all phases. It seems that these results related to the VFA accumulation in the ABR reactor.

Hydrogenotrophic bacteria have a major role in capturing hydrogen and electron to increase methane production. Recent studies have demonstrated that extra electrons could increase methane production and decrease hydrogen production in conventional AD reactor coupled MEC. Therefore, the activity of a collection of different bacteria as hydrogenotrophic methanogens, interacting with other bacteria might lead to a rise in methane production [33]. Pervious studies reported

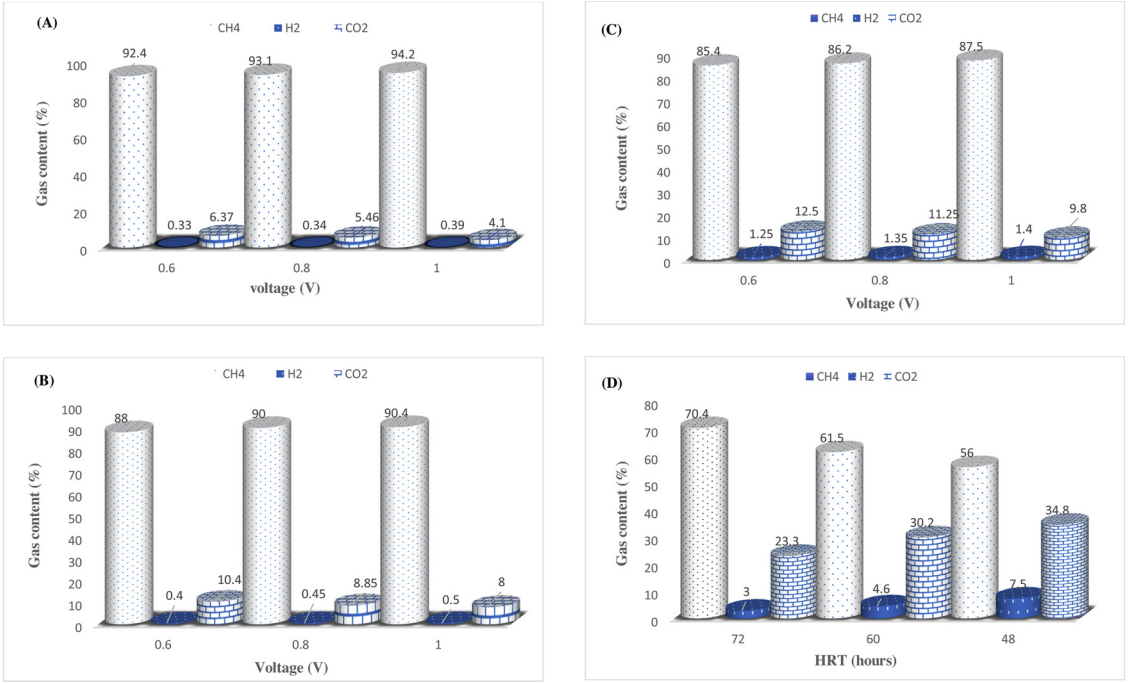

Fig. 8. Changes in the biogas content over the course of both reactors' performance. A (ABR-MEC reactor at HRT = 72 h), B (ABR-MEC reactor at HRT = 60 h), C (ABR-MEC reactor at HRT = 48 h) and D (ABR reactor at different HRTs).

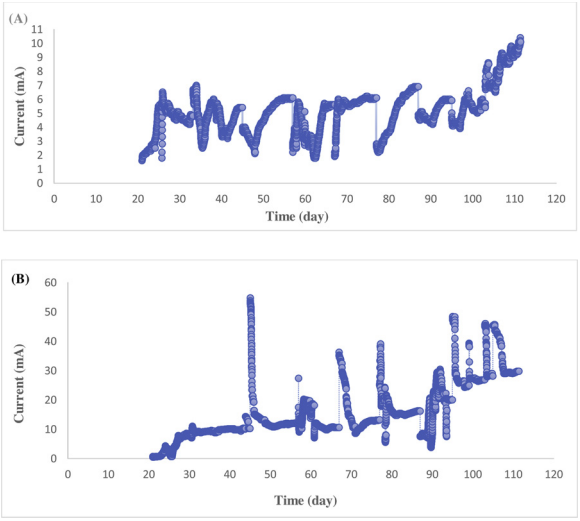

Fig. 9. The current profiles of the third compartment (C3) and fourth compartment (C4).

that hydrogenotrophic methanogens could use H_2 evaluated from cathode to convert CO_2 into CH_4 in bioelectrochemical systems ($4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$). In this study, hydrogen was detected in biogas during the whole process. The results show that the proportion of hydrogen gas in ABR-MEC reactor was lower than ABR reactor. Therefore, it seems that the increase of methane production is related to converting hydrogen.

3.6. Electrochemical properties of ABR-MEC at different phases

As it presented in Fig. 9, In phase II, the stable current in compartment 3 was obtained as 9,10.3, and 12.1 mA, on the voltage of 0.6, 0.8, 1.0, respectively at HRT of 72 h. The area of the carbon cloth was 42 cm^2 which meant the stable current density was 2.14, 2.45, 2.88 A/m^2. While this value in the compartment 4 under the applied voltages of 0.6, 0.8 and 1 V was 6.26, 9.69, 12.71 A/m^2. respectively. The current density of the last compartment was much larger than the third compartment of the ABR-MEC reactor throughout all phases. The coulombic efficiency (C_E) is the ratio of the electrons recovered as current relative to the total electrons available from substrate consumption [40]. As it presented in Fig. 9, the current profile showed a similar trend to COD removal rates increases. The results showed that increase voltage induced more oxidation of organic matter and followed by increase exoelectrogens activity and current production.

The Coulombic efficiency (C_E) production rate in the compartment 3 of the reactor, was very low. The highest C_E production was 12.6% in the compartment 3 and at current intensity of 10.1 mA. This shows that a major amount of oxidized organic compounds has been converted to methane gas, by methanogens process. In contrast, in compartment 4, the C_E production was higher than that of compartment 3. In the previous study, the presence of methanogens in the anode was reported as a reason for low C_E [35,41]. It seems that compartment 3 has a major role in the production of methane in ABR-MEC. The highest C_E production was 81.46% in the compartment 4, with a current intensity of 48.5 mA. Also, the results show that only a small segment of the oxidized organic compounds has been converted to the methane gas by methanogens process in the last compartment. As shown in Fig. 9, the current intensity at the ABR-MEC, is enhanced in each phase as increasing the applied voltage. Also, decreasing the HRT causes an increase in the current intensity, in both compartments.

The energy efficiency ($\eta_{electricity}$) is defined as the ratio of energy content of produced methane gas (W_{CH_4}) to the input electrical energy (W_E).The results show that energy efficiency in phase II was higher than the phase III and IV. The energy efficiency in phase II was 76%, 87.4% and 94.7% on the applied voltages of 0.6, 0.8 and 1 V, respectively, while, in phase III, it was 65.7%, 70.4% and 75.5% on the applied voltages of 0.6, 0.8 and 1 V respectively. Also, in phase IV, its value was 48.7%, 66.8%, and 69.1% on the applied voltages of 0.6, 0.8 and 1 V, respectively.

4. Conclusions

In this study, the performance of ABR-MEC and ABR reactor for treating a petrochemical wastewater was studied. So, the influence of two variables such as applied voltage and hydraulic retention time on COD removal, methane production rate, the content of methane, current profile, stability, alkalinity, VFA concentration, and pH level were determined. Regarding the results, the maximum COD removal efficiency in the ABR-MEC reactor was higher than that in ABR reactor, i.e. 96.5% versus 66.7%. Also, the maximum of yield CH_4 in ABR-MEC reactor was 1.4-fold than ABR reactor. Based on the results obtained from this study, the ABR reactor could not well the conversion of the intermediate products to methane at lower HRT, while the ABR-MEC reactor well consumes the intermediate products to methane at same HRTs. Thus, it can be concluded that there is an equilibrium between acid and methanogenic fermentation in this ABR-MEC reactor compared with ABR reactor. Considering these results, the energy efficiency had a range of 76% to 94.7% with an average of 86.7 % in phase II, which almost recovered most of the electrical energy input into the ABR-MEC reactor. All of these revealed that the ABR-MEC reactor has been operated successfully and could achieve the high methane production rate combined with wastewater treatment.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.bej.2019.01.021.

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