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Electrolysis enhanced anaerobic baffled reactor as retrofitting approach for molasses based distillery wastewater treatment

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ABSTRACT

This study evaluates the performance of electrolysis enhanced anaerobic baffled reactor (EABR), as an approach for retrofitting anaerobic unit treating molasses based distillery wastewater. For this purpose, a pilot with six chambers having total volume of 140 L was operated for more than 6 months inoculated with high-strength influent. Regarding the experimental results, the conventional anaerobic baffled reactor (ABR) could efficiently remove soluble chemical oxidation demand (COD) and volatile fatty acids (VFAs) to 90% and 92%, respectively. Here, the biogas productivity reached 0.96 $LL^{-1}d^{-1}$ in which methane constituted 70% and yielded 0.55 m^3/kg COD. However, this system showed instability and vulnerability in lower hydraulic retention time (HRT) below 3 d as a matter of pH reduction. The overall COD removal, biogas productivity and its methane content were limited to 40%, 0.25 $LL^{-1}d^{-1}$ and 45%, respectively. Therefore, the electrolysis cell was introduced in first chamber for retrofitting ABR. The EABR showed significant outcome in low HRT. This innovation could disintegrate the substrate and prevent pH from decline. Both could restore COD removal efficiency and biogas production to more than 70% and 0.6 $LL^{-1}d^{-1}$, respectively, in HRT of 1.5 d. Nevertheless, methane yield could not exceed 0.17 m^3/kg COD. Consequently, EABR was verified as an efficient approach and recovery strategy for controlling the adverse effects of low HRT, pH reduction or high organic loads in operation.

Keywords: Anaerobic baffled reactor (ABR); Distillery wastewater treatment; Electrolysis; Hydraulic retention time (HRT); Methane

1. Introduction

Conventional anaerobic baffled reactor (ABR) is identified as a promising solution for different wastewater treatment. This is a hydraulically based system that enforces the substrate to be in direct contact with the biomass via its compartmentalized configuration [1]. This formation provides an advantage for ABR. The microbial groups can partially be separated longitudinally down the reactor and make the operation more stable in regard [2]. In a review on recent developments, researchers have emphasized on this advantage and introduced ABR as an efficient approach for treating different substrates [3]. For example, in low-strength municipal wastewater, ABR showed high efficiency in practice as stand-alone [4,5] or preliminary unit

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[6]. In the latter, it has the potential of being followed by stabilization ponds [7], subsurface horizontal and vertical constructed wetlands [8], bio-rack wetlands [9], duckweed ponds [10], activated sludge [11] or membrane systems [12]. For industrial purposes, ABR is almost successfully passed the experimental studies. It is introduced as efficient system on treating the alcohol-containing desizing wastewater of textile industries [13], heavy oil and salty wastewater [14], swine wastewater [15], acidic zinc-containing wastewater [16], soybean protein processing wastewater [17], dilute aircraft de-icing fluid [18] and printing and dyeing wastewater [19]. This system is recently examined effectively for pulp and paper wastewater treatment in which the biodegradability of substrate is low and has considerable influence on anaerobic digestion [20]. Likewise, treating baker's yeast wastewater is also investigated as high-strength substrate in different hydraulic retention time (HRT) [21]. Its application is also recommended for decentralized wastewater treatment systems followed by membrane bioreactor (MBR) as energy-saving units for high-rise buildings [22].

In spite of ABR advantages in equalization of substrate through its compartmentalized configuration, reviews have explored that HRT and organic loads have extensive effects on its operation [23]. This is due to the fact that the performance of this system is reliant on solids hydrolysis in the first step [24]. It is observed and also simulated that the significant amounts of organics are removed in initial chambers where HRT can limit this performance [25,26]. Consequently, some literatures have focused on upgrading this system to retrofit ABR in low HRT [27]. Among these methods, using electrochemical application is recently considered for upgrading the anaerobic digestion. For instance, posttreatment unit based on electrocoagulation process is recommended for leachate treatment by hybrid ABR. This is expected to increase the efficiency of organics removal and biogas formation [28]. Likewise, the bio-electrochemical system is combined with ABR to develop the overall performance for organic removal. It is reported that this system may exceed 95% in chemical oxidation demand (COD) reduction. However, it is vulnerable to HRT or alkalinity variations [29]. The electrolytic cell is also used in anaerobic system to enhance the acidogenesis at short HRT below 3 h and prevent pH decline [30]. Before that, this technique is first patented in Iran and introduced for operation control of ABR treating dairy wastewater. Here, in laboratory scale, it is claimed that this can retrofit ABR against pH reduction in initial chambers. This is related to the formation of pH gradient inside the cell between cathode and anode that leads hydrogen out and reduces the partial pressure in regard [31]. This is consequently termed as electrolysis enhanced ABR (EABR) as previously used for similar systems before [32]. Yet, its performance and effects on organic removal is completely unknown for researchers particularly in high-strength wastewater treatment. Therefore, this paper intends to examine the performance of EABR treating high-strength wastewater of molasses based distillery effluent. Here, this approach is compared with the conventional configuration in pilot scale in high organic loads in which the COD removal efficiency, volatile fatty acid (VFA) digestion, methane formation and pH values are testified.

2. Materials and methods

2.1. Pilot setup

In order to carry out the experimental study, similar to the recent studies [33], a bench-scale ABR is setup and operated continuously for 156 d in the controlled temperature of 35°C using hot water bath as standard practices [34]. The main reactor is made of Plexiglas having 108 cm length, 26 cm width, 50 cm height and 10 mm thickness with total volume of 140 L. This system has equally six chambers constructed as standard practices [31]. The compartments are divided by vertical baffles having upflow-to-downflow parts by a ratio of 3:1 as recommended in literature [35]. The sampling and sludge discharge valves are, respectively, located on the side (with 30 cm distance from the bottom) and beneath. The biogas emitted from the whole system is directly discharged through the exhaust valves located on the top. Here, in order to test the electrolysis application, the first chamber is equipped with two electrodes. Anode is made of titanium coated with a mixed metal oxide of ruthenium and iridium while the cathode is a stainless steel electrode attached to a direct current electric source having 12 V and 2,000 mA as standard practices [36]. It should be noted that the electrolytic cell gets in line for a month intermittently with 2 h interval as recommended in previous studies [37]. Here, the electrodes have approximately 10 cm gap located in upflow part in which 5 cm is left over the surface and the remaining 30 cm is drowned. The electrolyte between the two electrodes is obviously the mixed emulsion of sludge and raw wastewater from the start-up period. The sludge is initially settled at the bottom of chambers while the upflow stream of wastewater rises the sludge up. This causes the emulsion within the two electrodes. The schematic design of EABR is shown in Fig. 1 [31].

2.2. Pilot start-up

The start-up was initiated with the batch mode by seeding the mixture of cow dung and sewage sludge at the ratio of 1:2 (50% v/V) in each compartment. The total volume of the seeded sludge was 85 L that was obtained from Isfahan wastewater treatment plant. This initially contained 3.4 gr/L total suspended solids and had theoretically 45 d retention time. The content of the reactor was recycled for homogeneity in the same period as per standard practices [9]. Afterward, the pilot has been continuously fed by peristaltic pumps from the real substrate (with soluble COD more than 8 g/L) from the equalization tank of the wastewater treatment plant of Alavijeh alcohol production industry. Here, the domestic wastewater

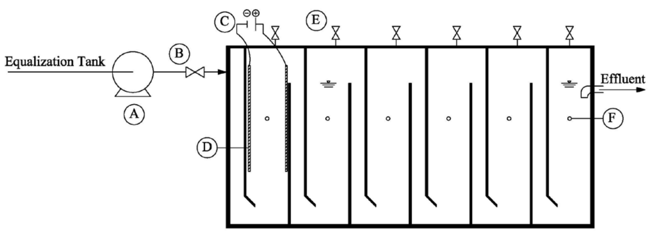

Fig. 1. EABR pilot configuration used in this study.
Note: A – peristaltic pump; B – control valve, C – electric source, D – electrode bars, E – gas exhaust valve, and F – sampling valve.

is mixed in preliminary units, and high dosages of carbonate calcium are added for alkalinity control [28,34]. The overall characteristics of influent are demonstrated in Table 1.

Since the influent COD is high, the organic loading rate (OLR) was controlled in start-up by increasing the HRT. OLR was maintained about 1.11 kg COD/m^{3}d for 3 months, and this reactor was operated at overall HRT of 8.3 d as an acclimatization period [33]. The start-up has been continued till the COD removal reached a constant level while the ratio of the VFAs to alkalinity in effluent decreased below 0.4 and became steady. By decreasing HRT to 2.4 d, OLR was gradually increased to 5 kg COD/m^{3}d. In this regard, the nominal sludge residence time (SRT) varied between 36 and 22 d. This was carried out to find the effect of HRT on the performance of ABR for COD removal and methane formation (S1). In the second step (S2), the electrolysis cell was turned on intermittently with 2 h interval for 1 month in which the reactor has been operated at previous conditions. Here, OLR was increased gradually with equal time steps from 4 to 10 kg COD/m^{3}d. This has made HRT between 2.4 and 1 d.

2.3. Sampling and tests

The whole samplings were performed weekly to analyze the soluble COD and pH in reactors through all compartments and the influent of the systems. The former is tested via titration method per standard method [38] while the latter is tested by multi-parameter device. The concentrations of VFAs are also tested weekly from the influent (first chamber) and effluent by gas chromatography (GC-Mass) in which the total values of acetic and propionic acids are reported [26]. The gas composition was also analyzed to find the percentage of CH_4 and CO_2 measured by GC using thermal conductivity detection (GC-TCD) as described in previous literature [31]. The samplings were repeated three times in each period. Thus, the weekly values of parameters are the average of these samples taken in a day. Here, it has been discussed that the overall efficiency is reliant on both internal indicators, such as pH and VFA removal, and external parameters like methane ratio of biogas and COD removal.

Table 1
Characteristics of influent and seeding sludge

Parameter	Value
Soluble COD, mg/L	9,693 ± 1,717
Total COD, mg/L	10,770 ± 1,910
Soluble BOD, mg/L	2,941 ± 999
Ammonia, mg/L	203 ± 69
Phosphate, mg/L	16 ± 5
C/N/P ratio	184/13/1
VFAs, mg/L	760 ± 343
pH	7.48 ± 1.1
TDS, mg/L	7,013 ± 1,877
TSS, mg/L	790 ± 530
MLSS, mg/L	12,340 ± 1,132
Alkalinity, mg $CaCO_3$/L	1,765 ± 247
Temperature, °C	35.2 ± 3.3

3. Results and discussion

Regarding the experimental results, it can be realized that ABR is an efficient system for treating molasses based distillery wastewater in high HRT. As shown in Fig. 1, it takes 45 d for start-up in which the soluble COD removal is stabilized on 90% similar to the result observed in hybrid ABR treating winery wastewater [39]. Here, in OLR of 1.1 kg COD/m^{3}d, the overall VFA digestion is also increased to more than 90% and became steady as observed previously for decentralized molasses wastewater treatment [40]. However, this efficiency is influenced by decreasing HRT. For instance, in average retention times of 5.6, 3.8 and 2.4 d, the SCOD removal efficiency decreases to 80%, 74% and 70%, respectively. It shows that in lower HRT, ABR can also be effective and reliable for primary treatment of molasses based distillery wastewater. Nonetheless, this system may not present suitable performance in HRT below 60 h. The experimental results have revealed that in these conditions, the organic removal efficiency can hardly exceed 40%. This may be due to the fact that in lower HRT, OLR increases. Here, high loads of biodegradable molasses would change the balance of anaerobic process to more acidogenesis and pH decline. In addition, the contact time for solid hydrolysis, degrading polysaccharides and VFAs digestion may not satisfy the required values [30]. Consequently, the process stops working unless some modifications are introduced. Here, EABR is proposed, as an innovative retrofitting approach, to increase the efficiency of system for organic removal in low HRT.

As illustrated in Fig. 2, using EABR intermittently may significantly increase the performance of reactor. The efficiency of EABR for SCOD removal in HRT of 2.4–1.5 d ranges from 83% to 67%. Comparing with the conventional system, it can be concluded that EABR can double COD removal in high OLRs. However, reducing HRT may still have influence on VFAs accumulation and consequently degrading the overall efficiency to less than 55% in 24 h retention time. Yet, the vulnerability of system against the hydraulic shock loads would be definitely reduced in comparison with conventional system as a matter of influent equalization by the electrolysis cell [31]. This verifies that EABR can increase the potential of organic removal and develop its reliability and stability for operation in low HRT.

In order to evaluate the performance of EABR in more detail, the SCOD removal within the compartments of reactor is shown in Fig. 3. Here, by reducing HRT from 8.3 d (S1-8.3) to 2.4 d (S1-2.4) in conventional ABR (first scenario), the overall

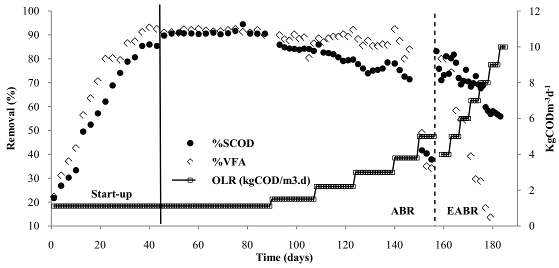

Fig. 2. Timeline of SCOD and VFA removal efficiency of ABR and EABR operated in different OLRs.

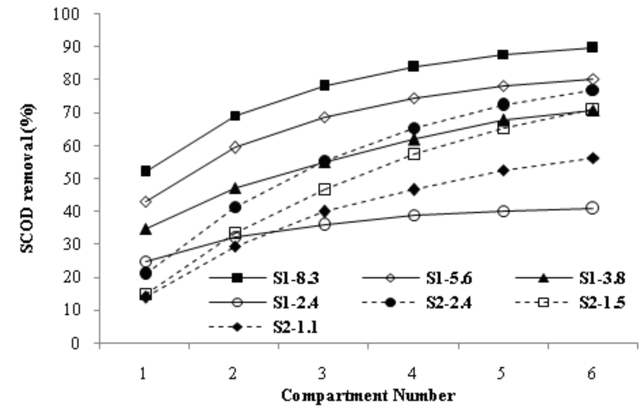

Fig. 3. SCOD removal in different scenarios throughout the reactor.

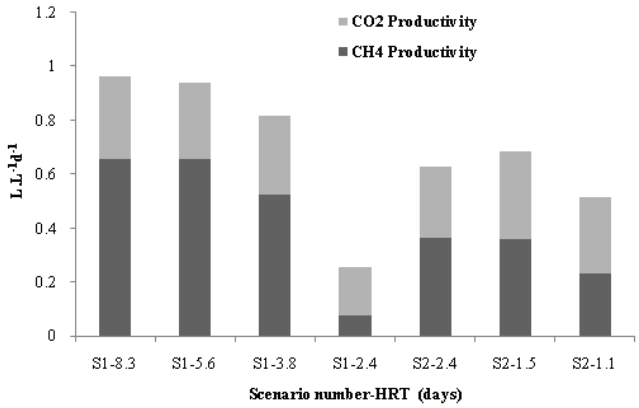

Fig. 5. Biogas production rates and their compositions in different tests.

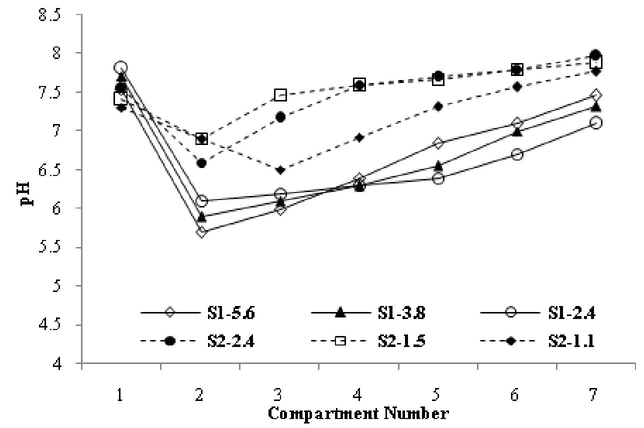

Fig. 4. pH values in different tests throughout the system.

organic removal efficiency is decreased throughout the system. This verifies that significant amounts of organic removal occur in the initial chambers. The subsequent compartments use the configuration of reactor to restore the efficiency back. Thus, it can be stated that in spite of the compartmentalized configuration of ABR for stabilizing the influent, the adverse effect of HRT reduction can be extended to the subsequent chambers. This trend is similarly observed in recent researches for municipal [26], and decentralized molasses wastewater treatment [40]. Nevertheless, using EABR in different HRT (S2-2.4, S2-1.5 and S2-1.1) can significantly increase the rate of SCOD removal in the second to the fourth chambers. As demonstrated in Fig. 3, this can be introduced as a recovery strategy for turning the reactor back for high performance. For instance, the overall organic removal efficiency of EABR with 2.4 and 1.5 d is rather equal to the ABR with 5.6 and 3.8 d retention time, respectively. These are, respectively, 77% and 71%. It may be due to the fact that in the first chamber, the electrolysis cell can disintegrate compounds into degradable materials with higher rates. This can expedite the hydrolysis step in regard. It can also simultaneously increase the pH level more rapidly in comparison with the conventional system (Fig. 4) and provide an opportunity for methanogenesis in further compartments [30]. It points to the fact that the process intervals between the hydrolysis, VFAs production and their digestion by methane forming bacteria are shortened in comparison with the conventional system. Here, lower HRT transfer the substrate more rapidly to the next chambers. Meanwhile, the electrolysis compensates the rate-limiting step of hydrolysis and simultaneously increases the pH level for methane formation. This reaction is recently termed as equalization step for methanogenesis in which the partial pressure of hydrogen can also be decreased by electrolysis [31]. As a result, this can swiftly retrofit the operation and performance of ABR treating high-strength molasses based distillery wastewater and may develop methane formation even in low HRT. In addition, it can be introduced as a recovery strategy for anaerobic process when long-chain fatty acid accumulates in initial chambers of ABR [41].

The analysis of biogas indicates that decreasing organic removal as a matter of HRT reduction has direct effect on biogas production (Fig. 5). The total values of biogas produced from the conventional ABR treating molasses based distillery wastewater are reduced from 0.96 $LL^{-1}d^{-1}$ (S1-8.3) to 0.25 $LL^{-1}d^{-1}$ (S1-2.4) in which the methane content is reduced from 70% to 30%, respectively. Here, in the steady state, the maximum methane yield per kg COD removal is calculated about 0.55 m^3/kg COD. This is similarly observed in previous research [42,43]. Yet, using EABR could restore biogas production in low HRT. In average, the total volumes of emitted biogas are calculated between 0.69 $LL^{-1}d^{-1}$ (HRT of 1.5 d) and 0.52 $LL^{-1}d^{-1}$ (HRT of 1.1 d). Here, the methane content ranges between 45% and 58% while its yield reaches to the maximum value of 0.17 m^3/kg COD. Lower yields of methane in comparison with ABR may be due to fact that organics are removed in EABR by different microbial groups while rapid disintegration of initial substrate may dominate more carbon dioxide in total biogas in regard. This can also be testified in further research by recent developments in modeling biogas production via fuzzy logic method [44].

Consequently, the biogas analysis confirms that using the electrolysis cell at the first chamber can promote the whole anaerobic process within the compartmentalized system of ABR. This leads into fast pH recovery, more organic removal efficiency and considerable biogas production. Consequently, EABR is approved as a promising approach for retrofitting conventional ABR treating high-strength wastewater. This innovation could reduce the vulnerability of system in high OLRs, increase its operating reliability and equalize the pH for the subsequent chambers. As a result, the COD removal efficiency and methane production were recovered. However, further studies are still required for its optimization with respect to the electrical arrangements, hydraulic specifications, energy outcomes and microbial analysis as discussed in similar studies [36].

4. Conclusion

This study is focused on performance evaluation of ABR and its modification by electrolysis cell (EABR) treating molasses based distillery wastewater. Here, it is revealed that the conventional ABR is only efficient on SCOD removal, VFA digestion and consequently methane production in HRT more than 4 d. In lower HRT, an adjustment is introduced in which the electrolysis cell is used in the first chamber. Regarding the experimental and comparative results, it can be concluded that using EABR may dramatically increase SCOD removal and biogas production rate in low HRT. This can be due to the electrolysis specifications on disintegrating compounds in low HRT and its capability on pH control. Consequently, this modification may extend the proper range of system operation to HRT below 48 h. In addition, this approach may add one step forward to find simple, practical and efficient approaches for increasing the reliability of these systems in operation. Moreover, it may present a perspective on stabilizing biogas production in industrial wastewater treatment plants.

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