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# Bioelectrochemical Cell (BeCC) integrated with granular activated carbon (GAC) in treating spent caustic wastewater: Effects of solid retention time (SRT) and organic loading rate (OLR)

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**Abstract.** The study aims to treat spent caustic wastewater by using a bioelectrochemical cell (BeCC) integrated with Granular Activated Carbon (GAC) as the bacterial attachment medium. BeCC is a bioelectrochemical reactor which employs microorganisms for substrates degradation and has the capacity to produce energy simultaneously. Microbial Fuel Cell (MFC) is also known as the bioreactor that could treat wastewater while producing energy. However, the BeCC reactor in the present study is more cost effective than an MFC reactor, since the BeCC was operated without the employment of a proton exchange membrane (PEM). The reactor was operated in a hybrid of anoxic and aerobic conditions whereby a baffle is used as the separator to minimize the oxygen transfer from the cathodic to the anodic side of the reactor. For enhancement of the BeCC performance, 10 g of suspended GAC was added into the BeCC reactor. The use of the suspended GAC is to allow higher surface area available for bacteria attachment. The study determined the best operating solid retention time (SRT) and organic loading rate (OLR) of BeCC in treating spent caustic wastewater and its performance throughout 30 days of operation was evaluated based on its Chemical Oxygen Demand (COD) removal and open circuit voltage (OCV). For SRT study, BeCC was tested at various SRT of range within 10 to 30 days whereas for OLR study, BeCC was tested at various OLR of range within 700 to 900 mg COD /L.d. From the study, the highest COD removal were 94.17% and 92.7% achieved at SRT of 30 days and OLR of 700 mg COD/L.d respectively. Whereas for energy recovery, the highest OCV were 336.4 mV and 362 mV achieved at SRT of 20 days and OLR of 800 mg COD/L.d respectively. Biochemical bacteria identification test was also carried out to identify the bacteria morphology attached on GAC in the BeCC at SRT of 20 days with 700 mg COD/ L.d of OLR and it is found that *Klebsiella Oxytoca* was the dominant bacteria attached on the GAC.

## 1. Introduction

This study presents the capacity of a BeCC integrated with GAC in treating spent caustic wastewater. Spent caustic wastewater was generally generated by the refineries and petroleum chemical plants and it is known as hazardous wastewater [1]. This type of wastewater has noxious properties as it contains harmful contaminants such as sulfide, mercaptans, phenol, sodium hydroxide, methanethiol, benzene and toluene [2, 3]. Spent caustic wastewater has high COD concentration influenced by its high sulfur content, high salinity and high alkalinity. Due to this properties, spent caustic wastewater required special



management before undergoing conventional as it is not easy to be treated, handled and disposed [1, 4]. It is reported that conventional treatment such as chemical oxidation and wet air-oxidation method often produce incomplete COD oxidation of spent caustic wastewater along with high operating costs and involved a considerable safety measures [3, 5]. Thus, the present study attempted to use biological method to serve as an effective alternative for complete COD degradation in treating spent caustic wastewater. Treating spent caustic wastewater by using biological method might be challenging as it might be limited by the high COD, alkalinity and salinity of the spent caustic wastewater [6], however, the method is feasible with spent caustic wastewater pre-treatments, biomass acclimation and sludge handling [1, 6].

A BeCC reactor integrated with GAC as the bacterial attachment medium is used in the present study to treat spent caustic wastewater. BeCC is a bioelectrochemical reactor which uses activated sludge for substrates degradation in spent caustic wastewater. While degrading the substrates, microorganisms also produces electron and protons which could be utilized for energy recovery of the system. Which means, not only that the spent caustic wastewater could be treated, but the reactor is also capable in producing energy simultaneously. This system has the same application as a Microbial Fuel Cell (MFC) reactor as an MFC is a bioreactor that uses bacteria as the biocatalysts to convert the bioenergy of biomass in wastewater into electrical energy [7]. A general MFC configuration would consists of an anode and cathode chamber, a proton exchange membrane (PEM) and electrodes submerged into the anode and cathode [8]. A PEM is generally required to only allow the transfer of protons from the anode to cathode compartment as well as to block fuels from the anode and oxygen from the cathode [9]. Nafion is the most common material employed as the PEM due to its highly selective permeability of protons [7]. However, this material is expensive [10] and also possessed high internal resistance which caused the power generation in MFC to be lowered [11]. The employment of Nafion as PEM in MFC has increased the MFC set up costs and has become a bottle neck problem in MFC [12]. Therefore, many researches attempted to investigate the substitute for Nafion by using a cheaper material [13]. Some of the material that has been tested were such as porcelain septum made from kaolin [14], earthen pot [15] and quartz sand chamber [16]. However, studies has also discovered PEMless MFC as a feasible in treating wastewater and energy recovery. In fact, better performance of a PEMless MFCs than the MFCs with a PEM was found as it was observed that the open circuit potential was higher when MFC was operated without a PEM and its power density was also observed to be increased. The same finding was obtained by Lee et al. (2015) in which MFC without PEM has increase both of the removal and energy recovery performance. Previous researches has shown the insignificant effect of PEM in MFC. Thus, this study presented the novel BeCC configuration without the employment of PEM as a cost effective method that has high potential in treating spent caustic wastewater and producing energy effectively.

As mentioned earlier, spent caustic wastewater is employed at the sample wastewater. Spent caustic wastewater is known for its noxious properties, thus it is difficult to be treated, handled and disposed [4]. It is reported that the treatment of spent caustic wastewater by using biological method requires spent caustic pretreatment, sludge acclimatization and sludge handling [6]. Therefore, in order to enhance bacteria survival in the spent caustic wastewater, the BeCC reactor was integrated with GAC as bacterial attachment medium. This is in aligned with previous research that found attached bacteria on GAC was more resistance to chlorination than the unattached bacteria [19]. This is the important feature of attached bacteria which facilitate the biomass adaptability and survival towards the noxious properties of the spent caustic wastewater. MFC integration with GAC has been widely conducted. However, most of the previous studies used GAC to act as electrode or adsorbent in MFCs. Unlike the previous MFC-GAC researches which integrated GAC in a packed bed form, the present study employed suspended GAC to be integrated with the BeCC system as in order to increase the surface area for biomass to attach. GAC is known for its highly porous and rough properties that would provide an appropriate surface for the attachment and growth of active biomass [20]. Therefore, GAC is chosen as the medium for biomass to attach in the present study. Besides improving the bacteria resistance towards toxicity, the attached bacteria was also reported to have higher growth rate than the unattached bacteria [21]. This condition allows the high biomass concentration in BeCC to be maintained. The integration of GAC in the present

study served to improve the biomass characteristics. Hence, effective spent caustic wastewater treatment and energy recovery of the BeCC could be achieved.

The BeCC used in the present study was inoculated with activated sludge that is consisting with mixed cultured bacteria. Mixed culture bacteria was preferred since pure culture bacteria is reported to be irrelevant for a bioelectrochemical system as it involved a considerable cost and is not practical for industrial effluent [22]. Besides that, spent caustic wastewater is the high strength wastewater that consists of stable content that are not readily biodegradable [23]. Thus, interactions of bacterial populations within the bacterial community is required for effective removal in spent caustic wastewater as it is reported that not all types of electrogens is able to fully oxidize several substrates [24] and some reported that that electrogenic bacteria in only capable in giving complete oxidation of simple substrates, thus development of cooperative interaction between the fermentative and the electrogens allowed the last ones to survive in the environment where only the complex substrates are available [25]. It is believed that the presence of both electrogenic and non-electrogenic bacteria populations in the mixed culture would contribute to better removal performance of BeCC. According to Asensio et al. (2017), the MFC culture is consisting of the electrogenic and non-electrogenic type and the enrichment of the electrogenic could prevent the performance of the bioreactor as an electrochemical cell [26]. Thus, biochemical bacteria identification was also carried out to identify the dominant bacterial population attached on the GAC.

The BeCC performance is also affected by a few parameters. Sludge age or known as solid retention time (SRT) is one of the important parameter involved. SRT is reported to be the parameter that controls the microorganisms growing in most of the bioprocesses system [27]. Generally in a bioreactor system, high SRT caused higher biomass accumulation and increased the MLSS concentration [27, 28]. Thus, higher SRT would be favored for higher substrates degradation. However, another research has reported that higher SRT would as well adversely affected the removal performance of a bioreactor and the condition was explained in terms of the formation of the pinpoint flocs at high SRT, which do not settle rapidly thus lead to higher suspended solid in the treated effluent, resulting in lower treatment efficiency [29]. In terms of the BeCC energy recovery, previous research reported that SRT would influences direct and indirect electron transfer mechanisms, and 95% of the total electricity production was contributed by the direct mechanisms [27]. In the present study, the best operating SRT for the BeCC integrated with GAC operation was determined as the presence of the attached cell would also influenced the SRT since there are variation in terms of the sludge age between the attached and suspended cells [30]. Besides that, the capacity of the BeCC integrated with GAC in treating spent caustic wastewater was further assessed by increasing its OLR. OLR is also one of the important parameter that affects biomass growth rate [31]. Previous MFC researches has shown that increase in OLR would decrease the removal performance as the biomass need to increase their quantity in order to balance with the food presence in the reactor. However, in terms of the removal performance, it is reported that high OLR is favorable due to higher microbial activity that improved the energy recovery [32]. According to Nam et al. (2010), different OLR resulted in different bacterial activity, internal resistance and cathode reaction limitation [33]. Thus, the present study also investigate the best operating OLR for the BeCC integrated with GAC operation in treating spent caustic wastewater.

## **2.0 Materials and Methods**

### *2.1 Wastewater preparation*

Spent caustic wastewater was collected from a petrochemical industry located in East Coast, Malaysia. Firstly, the wastewater was filtered to remove any solid particles and its pH was neutralized. The COD of wastewater was then adjusted to 700 mg/L by some pretreatments in order to create influent with suitable characteristics for biological treatment. The characteristics of the spent caustic wastewater is as shown in Table 1.

**Table 1.** Characteristics of spent caustic wastewater

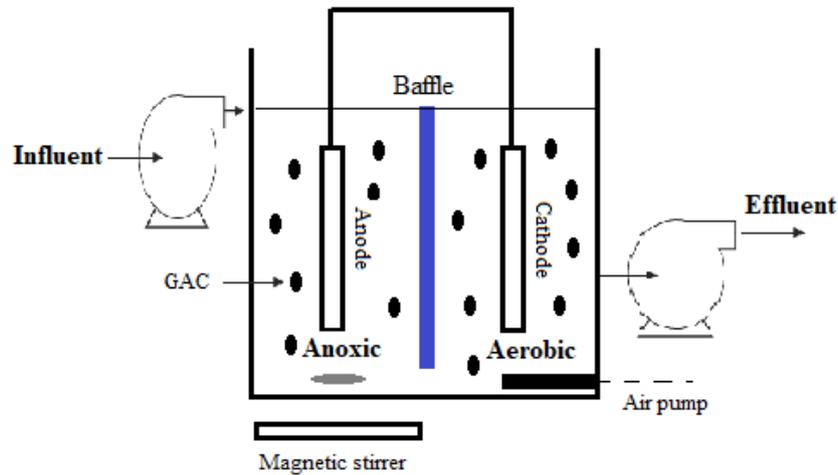
Parameter	Values
COD (mg/L)	700
BOD (mg/L)	70
Sulfide (mg/L)	0.085
Sulphate (mg/L)	66
Phosphate (mg/L)	3.8
Nitrate (mg/L)	14.6

### 2.2 Acclimatization

The BeCC was inoculated with 4L of activated sludge that was collected from the petrochemical industry located in East Coast, Malaysia. Acclimatization process is a required for the sludge to be adapted to the new environment. In the acclimatization process, the sludge was supplied with oxygen and was also fed with the prepared wastewater and glucose solution. The acclimatization period ended when the nutrient removal of the sludge achieved 80% and has constant MLVSS/MLSS ratio of higher than 60%.

### 2.3 BeCC operation

The BeCC reactor (L= 26.5 cm, H= 14.5 cm, W= 12 cm) used in the present study was made up from polycarbonate material was set up as shown in Figure 1. The reactor was designed as a membrane-less BeCC single chamber MFC with both electrodes submerged into the anodic and cathodic side of the reactor respectively. Oxygen is supplied at the cathodic side, and in order to reduce the oxygen transfer to the cathodic side, a baffle was used as the separator. On the other hand, in order to allow for protons transfer from the anodic to cathodic side of the reactor, the reactor was designed with a 0.2 cm gap between the baffle and the floor of the reactor. Previous study has stated that the use of a separator such as a baffle in a single a single chamber MFC reactor allowed fluid mixing in the anodic chamber while at the same time the oxygen diffusion to the cathode surface to be minimized [34]. The employment of the baffle has caused the reactor to be operated in anoxic and aerobic conditions at the anodic and cathodic side of the reactor respectively in which the oxygen concentration of the anoxic condition was controlled to be lower than 2 mg/L. Oxygen was supplied to the reactor by using an aeration pump and a magnetic stirrer is used to avoid sludge from sediment at the bottom. Graphite rods (L= 150 mm, D= 3 mm) was used as the anode and cathode electrodes.



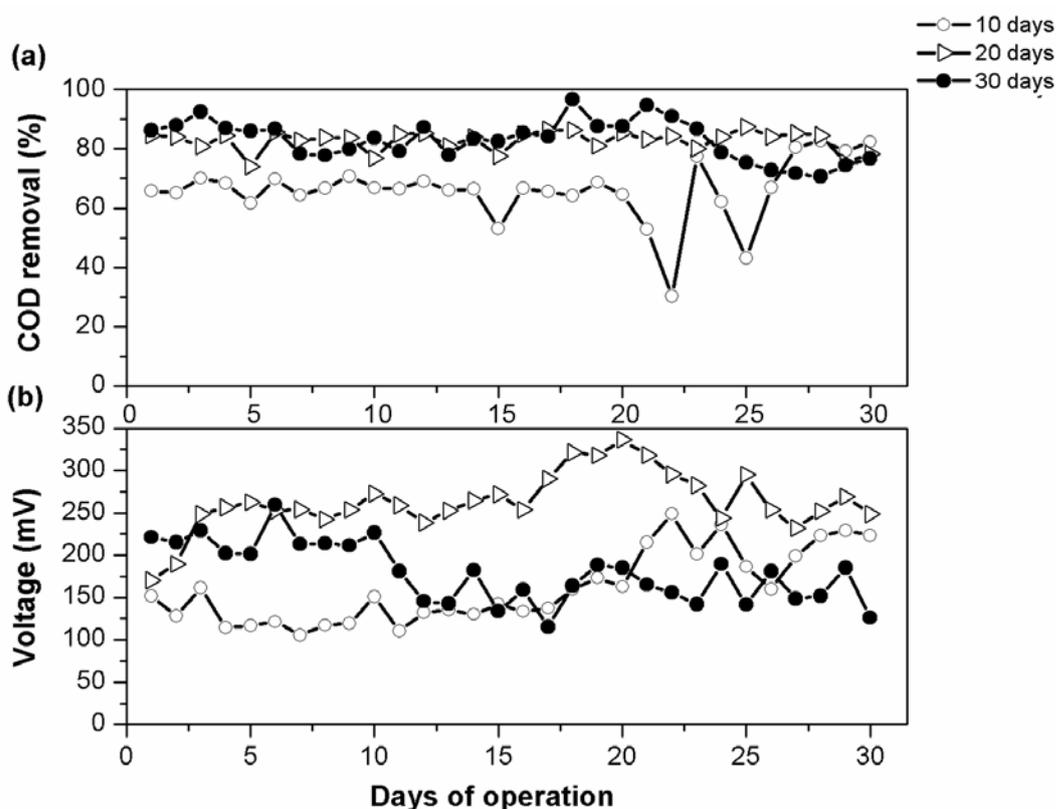
**Figure 1.** BeCC integrated with GAC set up

The reactor was inoculated with 4L activated sludge and 10 g of suspended GAC ( $6 \times 12$  mesh size) was added into the reactor for the BeCC biomass to attach. The SRT was controlled at 20 days of operation. The influent and effluent of the reactor was controlled with peristaltic pump in which the reactor was continuously supplied with wastewater at 0.2L/day. For the study of the effects of SRT, the BeCC was tested at different SRT of 10, 20 and 30 days by adjusting the biomass discharge flow rate. Whereas for the study of the effects of OLR, the BeCC was tested at different OLR of 700 mg/L, 800 mg/L and 900 mg/L by adjusting the effluent flowrate of the wastewater. The performance of the BeCC integrated with GAC was measured from its COD removal in which COD test was conducted based on standard APHA method [35]. Whereas, the BeCC energy recovery performance was evaluated from its OCV measured by using a multimeter.

### 3. Results and Discussions

#### 3.1 The Effects of SRT on COD removal and OCV

The performance of the BeCC integrated with GAC in terms of both wastewater treatment and energy recovery at different SRT was evaluated based on the COD removal and OCV generated. The result is as shown in Figure 2.



**Figure 2.** a) COD removal at different SRT versus days of operation. b) Voltage output at different SRT versus days of operation.

For the wastewater treatment efficiency, it is observed from Figure 2(a) that the highest COD removal was 94.17% achieved at SRT of 30 days whereas the lowest COD was 43.14% obtained at SRT of 10 days. The COD removal trend at SRT of 10 days was observed to be increasing with days of operation. It is also observed that the COD removal at SRT of 30 days was slightly higher than SRT of 20 days. The overall trend of the COD removal efficiency shows that COD removal was proportionally affected by SRT. SRT is basically the time spent by microorganisms in the reactor or the time available for the microorganisms to reproduce in the reactor [36]. Thus, higher removal at higher SRT was due to higher microorganism's concentration presence in the reactor at a prolonged SRT. The condition has led to high COD degradations and uptakes by microorganisms. The result of the present study is in aligned with previous MFC research which reported that high SRT produced better removal [27]. Besides that, it was agreed that there was a high cooperative interactions among the microbial population at higher SRT as according to D' Angelo et al (2017), higher SRT allowed the presence of more types of microorganisms in the biological culture of MFC [37]. Higher interaction among bacterial population is required for effective removal in spent caustic wastewater as spent caustic wastewater has stable contents that are not readily biodegradable [23], in which the stable content would be degraded by the by the last population that can survive in the environment where only complex substrates are available [25].

Low removal efficiency obtained at SRT of 10 days was explained in terms of its insufficient amount of microorganisms' presence for complete substrates degradation. The condition was due to higher discharge rate than the biomass growth rate at low SRT [36]. However, based on Figure 2(a), it is observed that as days of operation was increased, the COD removal were increased as well. The increase in the removal trend as days of operation was increased at SRT of 10 days was believed to be due to higher attachment of bacteria in the system at that point. The attached microorganisms might have higher

sludge age than the suspended GAC. The accumulation of the attached bacteria on GAC caused to bacteria be highly dense thus prevented the attached bacteria to be washed out from the system which means the attached bacteria could stay longer in the reactor despite being operated at low SRT. Besides that, attached bacteria also has higher growth rate than the suspended ones. This is in aligned with previous researches which reported that the attached cells on the surface of the GAC had higher rates of DNA synthetic activity than the cell grown in suspension [21]. The condition might be due to the nutrient availability at the GAC surfaces which facilitate the microbial adaptation and favor degradations [30]. Therefore, the increment in the COD removal as days of operation was increased at SRT of 10 days was agreed to be contributed by the attached biomass that has the capability to reproduce at a faster rate which led to higher biomass concentration in the reactor as days of operation was increased.

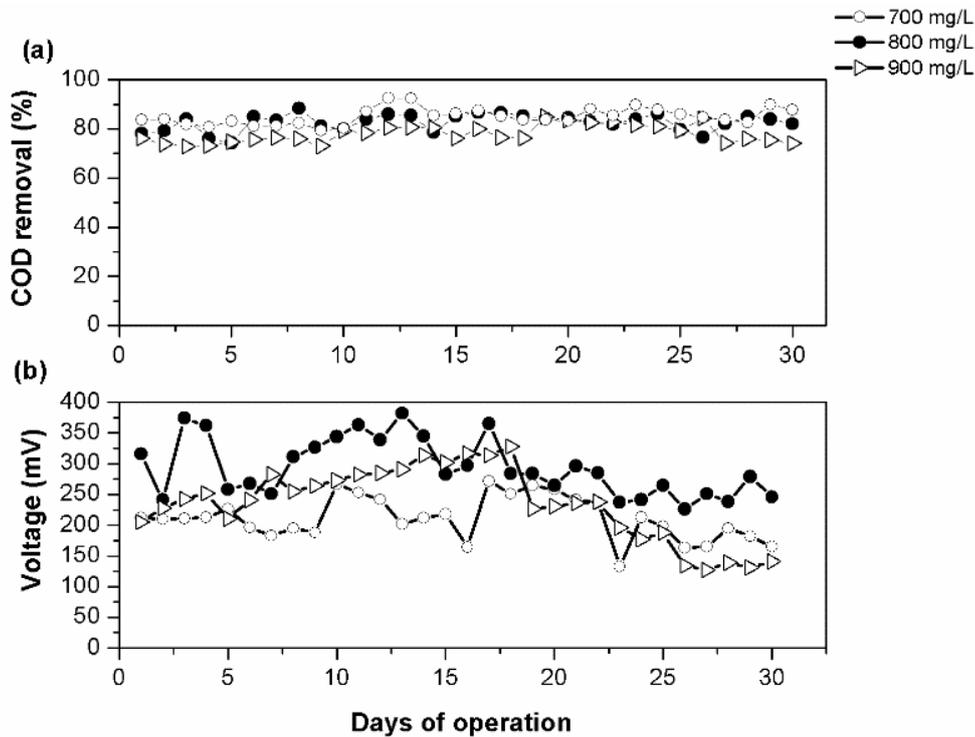
The BeCC integrated with GAC in terms of the energy recovery was evaluated based on its OCV and the result is shown in Figure 2(b). Based on the figure, it is shown that the highest OCV was 336.4 mV achieved at SRT of 20 days whereas the lowest voltage output was 105.6 mV achieved at SRT of 10 days. However, the voltage trend at SRT of 10 days is shown to be increasing with days of operation and was able to achieve its maximum OCV of 248.9 mV at day 22 of operation. Besides that, the result also demonstrated that SRT of 30 days also produced low OCV of 115.3 mV. And unlike the OCV trend at SRT of 10 days, the OCV trend at SRT of 30 days is showing a decreasing trend. It is shown that the highest achievable OCV for SRT of 30 days was 259.3 mV achieved at day 6 of operation. The overall trend of OCV with SRT was the increase in SRT from 10 to 20 days has increased the OCV, however, further increased of SRT beyond 20 days has decreased the OCV generated. Most often the energy recovery of a bioelectrochemical reactor was associated with the type of bacterial population in the reactor. Basically, the enrichment of the electrogenic culture may prevent the performance of the bioreactor as an electrochemical cell [26]. The same condition was believed to have occurred in the present study whereby the high OCV generated at SRT of 20 days was due to high electrogenic population presence at that point. This is in accordance with Mateo et al. (2017) which stated that when operating the MFC at high SRT, the different growth rate lead to mixed culture enriched with electrogenic microorganisms [27]. The increase in the electrogenic population at SRT of 20 days was agreed to be due to the faster growth rate of the electrogenic population than the competing microorganisms [37]. It was also believed that at this point, the dominant bacteria attached on the GAC was electrogenic type. This condition does not only improved the electrogenic microbial population, but its growth rate was also improved.

However, as the SRT was further increased to 30 days, the OCV was significantly dropped. The decline in the BeCC voltage at this point might be due to a few conditions such as the establishment of the slow growing bacterial population as SRT of 30 days allowed sufficient contact time for the bacteria to grow and reproduce which in turns has caused to overall bacterial population competitions for substrates. Therefore, it is concluded that high COD removal obtained at SRT of 30 days was mainly contributed by the non-electrogenic population. Since non-electrogenic bacteria is electrochemically inactive, it does not allow for electron transportations [38]. This scenario has inhibited efficient electron transfer at an elevated SRT, thus reducing energy recovery efficiency of the system. Operating MFC at high SRT increased the competitions for substrates [36]. Mateo et al. (2017) reported that at high SRT, the amount of microorganisms contained in MFC was sufficient to deplete the organic substrates contained in the fuel solution, however, the condition led to lack of organic substrates that cause difficulties for the electrogenic microorganisms to compete efficiently [27]. The result has indicated that SRT of 20 days is the best operating SRT for the BeCC integrated with GAC operation as lower SRT of 20 days is advantageous for the high growth rate and activity of the electrogenic population.

### *3.2 The effects of OLR on COD removal and OCV*

In the present study, the capacity of the BeCC integrated with GAC operation in treating spent caustic wastewater was further tested by varying its OLR in the range of 700 mg/L, 800 mg/L and 900 mg/L. Each operation with different OLR was carried out for 30 days of operation. The COD removal and the OCV generated were recorded and were shown in Figure 3. Based on Figure 3, the highest COD removal

was 92.7% achieved at OLR of 700 mg/L. The highest achievable COD removal for OLR of 800 mg/L and 900 mg/L were 88.4% and 84.9% respectively. From the present study, it was demonstrated that the best operating OLR for the BeCC was at OLR of 700 mg/L and the overall trend shows that increasing in OLR has decreased the BeCC removal efficiency.



**Figure 3.** a) COD removal at different OLR versus days of operation. b) Voltage output at different OLR versus days of operation.

The result obtained in the present study is consistent with most of the previous researches which reported that increased in OLR would decreased the removal performance. The result are consistent with previous research by Yu et al. (2012) whom reported that the increase in the COD loading rate resulted in a decreased in COD removal efficiency from 95.7% at 0.20 kg/m<sup>3</sup>/day to 80.5% at 0.40kg/m<sup>3</sup>/da [39]. Villasenor et al. (2013) conducted the operation of a horizontal subsurface flow constructed wetland integrated with microbial fuel cell in treating wastewater under different organic loading rates also reported that complete oxidization of organic matter in the wastewater was successful under low organic rates but not when being tested with high organic loading rates [40]. In the present study, it was agreed that the removal performance was associated with the F/M ratio of the system. Higher OLR has eventually resulted to higher F/M ratio which means that the food presence in the reactor was beyond the capability of the biomass to degrade, therefore, effective removal efficiency at higher OLR could not be achieved. Similar observation was made by Johir et al. (2012) in a membrane bioreactor system whereby it is reported that the biodegradation of the hydrophilic organic decreased with larger OLR resulted in an increased of F/M ratio which caused to higher organic concentration in the membrane bioreactor effluent [41]. However, it some cases, it is reported that high OLR could produce higher microorganisms, therefore higher organic degradation could be achieved. Higher microorganisms at high OLR might be contributed by the increment of easily degradable substrate as OLR was increased [30]. The condition observed by Arya et al. (2016) is in contrast with the present study, and the situation was agreed to be due

the stable contents in spent caustic wastewater that are not readily biodegradable [23]. Thus, increasing the OLR of the operation lead towards the presence of higher complex substrates that cannot be completely oxidized by the microorganisms, in turns reducing the removal efficiency at high OLR.

The energy recovery of the BeCC integrated with GAC operation at different OLR was compared based on its OCV and the result is shown in Figure 3(b). From the figure, it is shown that the highest OCV was 362 mV produced at OLR of 800 mg/L whereas the lowest OCV was 112 mV obtained at OLR of 900 mg/L. The highest achievable OCV at OLR of 700 mg/L and 900 mg/L were 324 mV and 226 mV respectively. The overall trend of the OCV with OLR shows that the increase in OLR of beyond 800 mg/L has caused the voltage output to be decreased. OLR is basically associated with hydraulic retention time (HRT). OLR is calculated as daily influent organic matter concentration divided by HRT [42] which means lower HRT would resulted in higher OLR. The increase in the OCV trend as the OLR was increased from 700 to 800 mg/L was believed to due to the increase of the sulfide content in the wastewater at higher OLR. Sulfide is one of the major content in spent caustic wastewater, thus increasing its OLR, increases the sulfide content as well. This is as reported by Hariz et al. (2013) whereby high COD in the wastewater was contributed by the sulfur content in the spent caustic wastewater [1]. Sulfide involvement in redox shuttle between biocatalyst and insoluble electron acceptor was also reported which means sulfide could as well act as a good electron donor [43]. High OLR provides higher sulfide content in the reactor, thus higher sulfide was utilized for energy recovery at OLR of 800 mg/L instead of at OLR of 700 mg/L. This is in aligned with a few of the previous MFC researches which also reported an improve in energy generation at higher OLR [42, 44]. A research conducted by Mansoorian et al. (2016) on catalyst-less and mediator-less membrane MFC in treating dairy wastewater at different OLR and reported that the maximum voltage was 856 mV produced at 53.22 kg COD/ m<sup>3</sup>d (high OLR). The condition was explained in terms of higher concentration of fuels provide sufficient substrate for electricity generation as when substrates was completely used, the voltage was gradually decreased [45].

Further increase of OLR to 900 mg/L has however caused the OCV value to drop and the condition was agreed to be caused by high OLR has provided nutrient efficiency to the competing microbes. According to He et al. (2005), higher OLR beyond the oxidation abilities of the anodophilic bacteria led to substrates oxidation by other microbes such as nitrate- reducing bacteria, sulfate- reducing bacteria or methanogenic archaea [46]. The side processes occurred by other types of competing microorganisms utilized electrons for their growth which diminished the electron quantity available for current generation [42]. Therefore, in the present study, adopting lower OLR of 800 mg/L is advantageous for electrogenic population and its activity. Nam et al. (2010) also the same trend of energy recovery efficiency with OLR whereby power density has decreased as OLR was increased and the condition was also explained in terms in terms of higher loading rates has encouraged the growth of non- electrogenic bacteria within the system [33]. Besides that, low OLR was also corresponded to higher HRT. Therefore, the high voltage output at OLR of 800 mg/L achieved in the present study was also associated with the HRT whereby adjusting the OLR to 800 mg/L instead of at OLR of 900 mg/L has allowed for higher contact time for the oxidation and reduction process to occur in the BeCC. Thus, high voltage output could be achieved. The result is parallel with previous MFC study that used animal carcass wastewater as sample wastewater and reported that longer contact time between biofilm and organic material in wastewater would benefits biofilms for the uptakes and degradation of substrates as well as for production and transfer of electrons onto the electrodes surfaces [47].

### 3.3 Biochemical Bacteria Identification

The BeCC integrated with GAC was operated at its best operating condition at SRT of 20 days and OLR of 700 mg/L. From the operation, the dominant bacteria attached on the GAC was identified by using biochemical identification method. From the result, it is found that the dominant bacteria attached on the GAC was *Klebsiella oxytoca*. *Klebsiella Oxytoca* is *K. pneumoniae* strains L17 (CCTCC AB 208106) was a gram-negative, facultative anaerobic iron-reducing bacterium. Under anaerobic condition, strain

L17 can metabolize fermentable substrates such as citrate, glycerol, glucose, and sucrose, and also can reduce hydrous ferric oxides such as goethite ( $\alpha$ -FeOOH), lepidocrocite and haematite [48]. It is believed that the presence of this bacteria as the dominant bacteria attached on the GAC has resulted to better removal and energy recovery performance of the BeCC in treating spent caustic wastewater. Previous study conducted by Islam et al. (2016) reported that *Klebsiella oxytoca* is an electrochemically active bacteria that showed better performance to generate electricity [49]. *K. pneumoniae* biofilm cell was also reported to be responsible for direct electron transfer from fuels to electrode during electricity production. This bacteria has also contributed in treating spent caustic wastewater, as it is also reported that this bacteria strain can run various fuels, from simple molecule glucose to complex molecule starch [50].

#### 4. Conclusion

The study presented the potential of BeCC integrated with GAC i.e. 10 g of suspended GAC as an effective treatment in treating spent caustic wastewater and energy recovery. In the study, the best operating SRT and OLR were investigated. For the study of the best operating SRT in which the operation was tested at 10, 20 and 30 days, it is found that the highest COD removal was 94.17% achieved at SRT of 30 days whereas the highest OCV generated was 336.4 mV achieved at SRT of 20 days. The condition was explained in terms of higher contact time for reproduction and growth at high SRT which contributed towards high amount of microorganisms.

For the study of the best operating OLR of the BeCC, the highest COD removal was 92.7% achieved at OLR of 700 mg/L whereas the highest OCV generated was 362 mV obtained at OLR of 800 mg/L. In terms of removal efficiency, the condition was explained to be due higher complex substrates in the reactor at high OLR that is beyond the biomass capability to produce complete substrates degradation. Whereas in terms of the energy recovery, high OLR has favored the growth of the non- electrogenic population which caused to inefficient electron transfer at high OLR. Last but not least, for biochemical bacteria identification operated at its best operating condition of SRT 20 days and OLR of 700 mg/L, it is found that the dominant bacteria attached on the GAC was *Klebsiella oxytoca*, an electrochemically active bacteria that contributed towards better removal and energy recovery of the BeCC.

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## References

- [1] Hariz, I.B., et al., *Treatment of petroleum refinery sulfidic spent caustic wastes by electrocoagulation*. Separation and Purification Technology, 2013. **107**: p. 150-157.
- [2] Alnaizy, R., *Economic analysis for wet oxidation processes for the treatment of mixed refinery spent caustic*. Environmental Progress & Sustainable Energy, 2008. **27**(27): p. 295-351.
- [3] Veerabhadraiah, G., N. Mallika, and S. Jindal, *Spent caustic management: Remediation review*. Hydrocarbon Processing, 2011. **90**: p. 1-14.
- [4] Hawari, A., et al., *A comparative study of the treatment of ethylene plant spent caustic by neutralization and classical and advanced oxidation*. J Environ Manage, 2015. **151**: p. 105-12.
- [5] de Graaff, M., et al., *Biological treatment of refinery spent caustics under halo-alkaline conditions*. Bioresour Technol, 2011. **102**(15): p. 7257-64.
- [6] Vaiopoulou, E., et al., *Electrochemical sulfide removal and caustic recovery from spent caustic streams*. Water Res, 2016. **92**: p. 38-43.
- [7] Du, Z., H. Li, and T. Gu, *A state of the art review on microbial fuel cells: A promising technology for wastewater treatment and bioenergy*. Biotechnol Adv, 2007. **25**(5): p. 464-82.
- [8] Tekle, Y. and A. Demeke, *Review on microbial fuel cell*. Basic Research Journal of Microbiology, 2015. **2**(1): p. 5.
- [9] Wu, C.-H., et al., *Feasibility study of electricity generation and organics removal for a molasses wastewater by a waterfall-type microbial fuel cell*. . Journal of the Taiwan Institute of Chemical Engineers, 2017. **78**: p. 150-156.
- [10] Yousefi, V., D. Mohebbi-Kalhari, and A. Samimi, *Ceramic-based microbial fuel cells (MFCs): A review*. International Journal of Hydrogen Energy, 2017. **42**(3): p. 1672-1690.
- [11] Parkash, A., *Microbial Fuel Cells: A Source of Bioenergy*. Journal of Microbial & Biochemical Technology, 2016. **8**(3).
- [12] Kalathil, S., J. Lee, and M.H. Cho, *Granular activated carbon based microbial fuel cell for simultaneous decolorization of real dye wastewater and electricity generation*. N Biotechnol, 2011. **29**(1): p. 32-7.
- [13] Ghadge, A.N. and M.M. Ghangrekar, *Performance of low cost scalable air-cathode microbial fuel cell made from clayware separator using multiple electrodes*. Bioresour Technol, 2015. **182**: p. 373-7.
- [14] Park, D.H. and J.G. Zeikus, *Improved fuel cell and electrode designs for producing electricity from microbial degradation*. Biotechnol Bioeng, 2003. **81**(3): p. 348-55.
- [15] Behera, M., P.S. Jana, and M.M. Ghangrekar, *Performance evaluation of low cost microbial fuel cell fabricated using earthen pot with biotic and abiotic cathode*. Bioresour Technol, 2010. **101**(4): p. 1183-9.
- [16] Gao, C., et al., *Development of a novel carbon-based conductive membrane with in-situ formed MnO<sub>2</sub> catalyst for wastewater treatment in bio-electrochemical system (BES)*. Journal of Membrane Science, 2018. **549**: p. 533-542.
- [17] Liu, H. and B.E. Logan, *Electricity Generation Using an Air-Cathode Single Chamber Microbial Fuel Cell in the Presence and Absence of a Proton Exchange Membrane*. Environmental Science and Technology, 2004. **38**: p. 4040-4046.
- [18] Rahimnejad, M., et al., *A review on the role of proton exchange membrane on the performance of microbial fuel cell*. Polymers for Advanced Technologies, 2014. **25**(12): p. 1426-1432.
- [19] LeChevallier, M.W., et al., *Disinfection of Bacteria Attached to Granular Activated Carbon*. Applied and Environmental Microbiology, 1984. **48**(5): p. 918-923.
- [20] Muhamad, M.H., et al., *Comparison of the efficiencies of attached- versus suspended-growth SBR systems in the treatment of recycled paper mill wastewater*. J Environ Manage, 2015. **163**: p. 115-24.
- [21] Davies, D.G. and G.A. Mcfeters, *Growth and Comparative Physiology of Klebsiella oxytoca Attached to Granular Activated Carbon Particles in Liquid Media*. . Microbial Ecology, 1988. **15**: p. 165-175.
- [22] Huarachi-Olivera, R., et al., *Bioelectrogenesis with microbial fuel cells (MFCs) using the microalga Chlorella vulgaris and bacterial communities*. Electronic Journal of Biotechnology,

2018. **31**: p. 34-43.
- [23] Seyedin, S.H. and M. Hassanzadeganroudsari, *The Efficient Process for Spent-caustic Wastewater Treatment*. International Journal of Advanced Research in Science, Engineering and Technology, 2018. **5**(2): p. 5284-5288.
- [24] Fedorovich, V., et al., *Novel electrochemically active bacterium phylogenetically related to *Arcobacter butzleri*, isolated from a microbial fuel cell*. Appl Environ Microbiol, 2009. **75**(23): p. 7326-34.
- [25] Rodrigues, D.S., *Microbial Community Optimization for Electricity Generation in Microbial Fuel Cells*, in *Biological Engineering*. 2014, Instituto Superior Tecnico, Portugal.
- [26] Asensio, Y., et al., *Selection of cheap electrodes for two-compartment microbial fuel cells*. Journal of Electroanalytical Chemistry, 2017. **785**: p. 235-240.
- [27] Mateo, S., et al., *The influence of sludge retention time on mixed culture microbial fuel cell start-ups*. Biochemical Engineering Journal, 2017. **123**: p. 38-44.
- [28] Mutamim, N.S.A. and Z.Z. Noor, *Assessment of Membrane Bioreactor in Treating Spent Sulfidic Caustic Wastewater: Effects of Organic Biomass Concentration and Solid Retention Time*. Chemical Engineering Research Bulletin, 2017. **19**: p. 102-110.
- [29] Tremblay, A., R.D. Tyagi, and R.Y. Surampalli, *Effect of SRT on Nutrient Removal in SBR system*. Practice Periodical of Hazardous, Toxic and Radioactive Waste Management 2015: p. 183-90.
- [30] Arya, V., L. Philip, and S.M. Bhallamudi, *Performance of suspended and attached growth bioreactors for the removal of cationic and anionic pharmaceuticals*. Chemical Engineering Journal, 2016. **284**: p. 1295-1307.
- [31] Behera, M. and M.M. Ghangrekar, *Performance of microbial fuel cell in response to change in sludge loading rate at different anodic feed pH*. Bioresour Technol, 2009. **100**(21): p. 5114-21.
- [32] Prasertsung, N. and C. Ratanatamskul, *Effects of organic loading rate and operating temperature on power generation from cassava wastewater by a single-chamber microbial fuel cell*. Desalination and Water Treatment, 2013. **52**(4-6): p. 937-946.
- [33] Nam, J.Y., et al., *Effects of organic loading rates on the continuous electricity generation from fermented wastewater using a single-chamber microbial fuel cell*. Bioresour Technol, 2010. **101 Suppl 1**: p. S33-7.
- [34] Hu, Z., *Electricity generation by a baffle-chamber membraneless microbial fuel cell*. Journal of Power Sources, 2008. **179**(1): p. 27-33.
- [35] APHA, *Standard Methods for the Examination of Water and Wastewater*. 2005, United Book Press Incorporation: Baltimore, Maryland,.
- [36] Penteado, E.D., et al., *Influence of sludge age on the performance of MFC treating winery wastewater*. Chemosphere, 2016. **151**: p. 163-70.
- [37] D'Angelo, A., et al., *Optimization of the performance of an air-cathode MFC by changing solid retention time*. Journal of Chemical Technology & Biotechnology, 2017. **92**(7): p. 1746-1755.
- [38] Debabov, V.G., *Electricity from microorganisms*. Microbiology, 2008. **77**(2): p. 123-131.
- [39] Yu, J., et al., *Electricity generation and microbial community in a submerged-exchangeable microbial fuel cell system for low-strength domestic wastewater treatment*. Bioresour Technol, 2012. **117**: p. 172-9.
- [40] Villasenor, J., et al., *Operation of a horizontal subsurface flow constructed wetland--microbial fuel cell treating wastewater under different organic loading rates*. Water Res, 2013. **47**(17): p. 6731-8.
- [41] Johir, M.A.H., et al., *Effect of organic loading rate on organic matter and foulant characteristics in membrane bio-reactor*. Bioresource Technology, 2012. **113**: p. 154-160.
- [42] Capodaglio, A.G., et al., *Role of operating conditions on energetic pathways in a Microbial Fuel Cell*, in *International Conference on Technologies and Materials for Renewable Energy, Environment and Sustainability, TMREES15*. 2015, Elsevier Ltd. p. 728-735.
- [43] Dutta, K.P., et al., *Role of Sulfur during Acetate Oxidation in Biological Anodes*. Environmental Science and Technology, 2009. **43**: p. 3839-3845.

- [44] Kim, H., et al., *Effect of organic loading rates and influent sources on energy production in multi-baffled single chamber microbial fuel cell*. Desalination and Water Treatment, 2014. **56**(5): p. 1217-1222.
- [45] Mansoorian, H.J., et al., *Evaluation of dairy industry wastewater treatment and simultaneous bioelectricity generation in a catalyst-less and mediator-less membrane microbial fuel cell*. Journal of Saudi Chemical Society, 2016. **20**(1): p. 88-100.
- [46] He, Z., S.D. Minteer, and L. Angenent, *Electricity Generation from Artificial Wastewater Using an Upflow Microbial Fuel Cell*. Environmental Science Technology, 2005. **39**: p. 5262-5267.
- [47] Li, X., et al., *Animal carcass wastewater treatment and bioelectricity generation in up-flow tubular microbial fuel cells: effects of HRT and non-precious metallic catalyst*. Bioresour Technol, 2013. **128**: p. 454-60.
- [48] Deng, L., et al., *A study of electron-shuttle mechanism in Klebsiella pneumoniae based-microbial fuel cells*. Chinese Science Bulletin, 2010. **55**(1): p. 99-104.
- [49] Abdul Karim, Z.A., et al., *Performance of Klebsiella oxytoco generate electricity from POME in microbial fuel cell*. MATEC Web of Conferences, 2016. **38**.
- [50] Zhang, L., et al., *Microbial fuel cell based on Klebsiella pneumoniae biofilm*. Electrochemistry Communications, 2008. **10**(10): p. 1641-1643.