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Microbial Fuel Cell (MFC) in treating spent caustic wastewater: Varies in Hydraulic Retention Time (HRT) and Mixed Liquor Suspended Solid (MLSS)

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ABSTRACT

The performance of an anoxic-aerobic MFC reactor operated with spent caustic wastewater was studied at different HRT and MLSS. Spent caustic wastewater is the industrial wastewater with high COD concentration influenced by its high sulfur content, high salinity and high alkalinity. Little is known on the MFC capacity in treating spent caustic wastewater, therefore the present study employed spent caustic wastewater as the feed wastewater. The MFC performance was evaluated in terms of voltage production, COD and sulfide removal efficiency. The HRT range tested were 7 days, 8 days and 9 days whereas the MLSS range tested were 1500 mg/L, 2000 mg/L and 2500 mg/L. From the study, HRT of 9 days was the optimum HRT for the MFC operation with the highest COD and sulfide removal efficiency of 98% and 98.98% respectively. The removal efficiency increased with increasing HRT. In terms of voltage production, the highest achievable voltage was 82.1 mV obtained at HRT of 9 days. The overall energy production trend shows that energy production was increased with increasing HRT. For MLSS study, the optimum MLSS for the MFC operation was at 1500 mg/L with the highest COD removal and sulfide removal efficiency of 94.07% and 89.01% respectively. In terms of voltage production, the highest achievable voltage was 36.7 mV obtained at MLSS of 2500 mg/L.

1. Introduction

MFC is an emerging technology to directly extract energy from wastewater through microorganisms metabolism [1]. According to Logan et al. [2], MFC is a bioreactor that can convert the biomass energy in the wastewater into electrical energy [2]. This method employs microorganisms as biocatalysts to catalyze the oxidation and reduction reactions occur at the anode and cathode compartment [3]. While oxidizing the substrates, microorganisms generates protons and electrons. The transfer of the protons and electrons to the cathode generates electricity [3,4]. Therefore, both of the wastewater treatment and energy recovery could be achieved by using this method. Many researchers have shown interest in MFCs technology as this technology has the potential to solve the water pollution and natural exhaustion problems simultaneously.

In the present study, anoxic-aerobic MFC reactor was used to treat spent caustic wastewater. Spent caustic wastewater is hazardous industrial wastewater that is mainly produced from the refineries and petroleum chemical plants [5]. Spent caustic wastewater is named after the wasted or used caustic soda. [6,5]. Caustic soda is the sodium hydroxide solution that is used as the scrubbing agent in the desulphurisation process to remove different gases including hydrogen sulfide and carbon dioxide from different hydrocarbon streams [7]. During the process, hazardous gaseous react with the sodium hydroxide solutions, hydrogen sulfide and thiols contaminants are then absorbed producing a waste solution known as the spent caustic [8,5]. The waste solution is in dark brown to black colour as it contains other toxic organosulfur and aromatic compounds as well such as methanethiol, benzene, toluene and phenol [9]. Spent caustic wastewater has high COD concentration influenced by its high sulfur content, high salinity and high alkalinity [10]. Because of these properties, spent caustic wastewater is not easy to be treated, handled and disposed. It is reported that spent caustic wastewater requires special management before undergoing conventional wastewater treatment [5].

The conventional treatment methods of spent caustic wastewater are such as chemical oxidation process and wet air oxidation (WAO). The conventional treatment methods of spent caustic wastewater are often reported to produce incomplete oxidation of substrates and involved high operating risks. Example of the commonly used chemical oxidant in the chemical oxidation process is hydrogen peroxide.

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Nomenclature

BOD	Biochemical oxygen demand
COD	Chemical oxygen demand
F/M	Food to microorganisms ratio
HRT	Hydraulic Retention Time
MFC	Microbial Fuel Cell
MLSS	Mixed liquor suspended solid
MLSVSS	Mixed liquor volatile suspended solid
OLR	Organic loading rate
PEM	Proton exchange membrane
PTA	Purified terephthalic acid
SRT	Solid retention time
WAO	Wet air oxidation

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Hydrogen peroxide possesses high oxidation potential in which it can oxidizes most of the organic and inorganic compound, however, the reaction involved high risks of explosion and high operating cost [11]. It is also reported that chemical oxidation with hydrogen peroxide often gives incomplete oxidation of the dissolved sulfide to thiosulfate. Plus, the storage and handling of hydrogen peroxide is associated with considerable safety measures [12]. Other treatment method such as wet air oxidation (WAO) is also reported to give incomplete reduction of COD because carboxylic acid is formed and resist further oxidation. Unlike MFC treatment method, the conventional treatment methods of spent caustic wastewater are not utilizing the capacity to produce renewable energy from the wastewater treatment. It is reported that contaminants such as sulfide, ammonia, nitrite, perchlorate, chlorinated compounds, copper, mercury and iron could be effectively removed by using MFCs application [13,14]. Therefore, MFC could be a highly potential method to be used in treating spent caustic wastewater effectively while producing electricity.

The performance of MFC is affected by many factors such as types of configuration [15], source of substrates [16], temperature [17], pH [18], electrode materials [19] and other operating conditions such as Solid Retention Time (SRT) [20], Hydraulic Retention Time (HRT) [21], Mixed Liquor Suspended Solid (MLSS) concentration, Organic Loading Rate (OLR) [22] and etc. In the MFCs application, wastewater served as the substrates that provide nutrient for the cell [23]. According to [24] wastewater with moderate to high organic content can be exploited as the MFCs substrates [24]. It is reported that there are different types of organic matter presence in different type of wastewater in which resulted in dissimilarities in their biodegradability and affecting the COD removal rate [25]. In terms of energy production, it is reported that power densities could be improved by using higher strength of wastewater such as brewery and animal wastewater [16]. However, high strength wastewater required longer treatment duration than domestic wastewater to ensure good quality of effluent [16]. MFC performances had been reported to be successful in treating various types of wastewater such as domestic wastewater [26–28], swine wastewater [29], agro food wastewater [30], artificial wastewater [31], synthetic wastewater [32–34], fruit processing wastewater [35], tannery wastewater [4], brewery wastewater [36] and etc. However, to the best our knowledge, little is known on the MFC's capacity in treating high strength spent caustic wastewater. Previous research conducted by [37] on MFC electro-biocatalytic treatment operated with petroleum refinery wastewater reported that the system was able to achieve 84.4% of substrate degradation when being operated in continuous mode and 81% when being operated in batch mode with highest energy production of 225 mW/m^2. Another research operated a membrane-less single chamber MFC by using raw wastewater of Purified Terephthalic acid (PTA) i.e. a raw material for petrochemical products reported that the system achieved 31.8 mW/m^2 with 74% of COD removal efficiency [38]. These previous researches demonstrate MFC technology as one of the potential method in treating spent caustic wastewater. Therefore, continuous investigations on the possibility of MFCs application to provide effective treatment of spent caustic wastewater should be conducted.

In the present study, the performance of anoxic-aerobic MFC in treating spent caustic wastewater was also investigated at different HRT and MLSS concentration. HRT is the amount of time in hours for wastewater to pass through a tank e.g. aeration tank [39]. Generally, for a membrane bioreactor system, high HRTs are suitable to be applied for wastewater with high COD, BOD and slowly biodegradable compounds [40]. According to [16], MFCs application on treatment of low strength wastewater is effective at HRTs similar to aerobic process. However, a higher HRT is required for high strength wastewater [16]. From the previous research, it was expected that the MFC operation in present study could achieve better removal performance at higher HRT as the system employed high strength spent caustic wastewater for its operation. In terms of energy production, previous research on MFCs operated with domestic wastewater conducted by [41] reported that a stable voltage output could be achieved at low HRT [41]. Another research of MFC using domestic wastewater as substrates by [42] observed that energy production was decreasing with increasing HRT [42]. The scenario was explained in terms of reduction in cell metabolism due to decrease of substrate concentration at low HRT. MLSS is also one of the important parameters affecting the performance on MFC. MLSS is the concentration of the suspended solids in the mixed liquor. MLSS is generally taken as index of the mass of active microorganisms in the aeration tank. It is reported that the typical MLSS range for conventional activated sludge process for wastewater treatment is within 2000–4000 mg/L [43]. However, the anoxic-aerobic MFC is not fully working as the conventional activated sludge system due to some modifications such as the cathode side was exposed to air unit and the system involved oxidation and reduction reactions. Thus, a little deviation with the conventional activated sludge process in terms of its ideal MLSS value was expected. In terms of removal efficiency, it is reported that increase in MLSS concentration indicates low F/M ratio in which could improved the removal efficiency [44]. However, another research reported that increase in MLSS concentration would decrease the removal efficiency as the decrease in F/M ratio would cause the microorganisms' activity to be reduced, in turn reducing removal efficiency as well [45]. In terms of energy production, it is reported that low MLSS would contribute to higher energy production as at lower MLSS, higher rate of oxygen consumption was achieved [46]. Further studies on MFC technology should be conducted for its effective wastewater treatment and energy recovery. Therefore, the present study aims to investigate the effects of HRT and MLSS concentration on the anoxic-aerobic MFC performance in terms of its COD and sulfide removal efficiency as well as the voltage production in treating spent caustic wastewater.

2. Materials and method

2.1. Wastewater preparation

Spent caustic wastewater was obtained from a petrochemical industry located in Gebeng, Kuantan. The COD and sulfide concentration of the wastewater were determined by using APHA standard method [47]. For COD test, the mixture of sample and COD reagent was placed in DRB-200 reactor (HACH®, USA) to be preheated at 150 °C for 2 h. Both of the COD and sulfide concentration were measured by using DR2800 UV–vis Spectrophotometer DR2800 (HACH®, USA). The concentration of the influent wastewater was then designed with COD and sulfide concentration within the range of 400 mg/L and 80–100 μg/L. The adjustment was made in order to create wastewater influent that has characteristics for biological treatment. According to [48], the waste to be used for biological purpose need to be applied with dilution factors up to three in order to reduce the pH and sodium level down to acceptable concentration for neutrophilic sulfide- oxidizing bacteria [48]. Sodium acetate was also added into the wastewater prepared as additional source of nutrients for bacteria [49].

2.2. Acclimatization

Acclimatization is the process that allows bacteria's adaptation to new environment [50]. In the study, the sludge was acclimatized until the biomass was able to remove 80% of nutrients and achieved more that 60% of MLVSS/MLVSS ratio indicating the sludge ability to adapt in the new environment.

2.3. MFC operation

A 4L anoxic aerobic MFC reactor was used for the study. The MFC reactor was inoculated with aerobic sludge and was operated in continuous mode at HRT and SRT of 20 days. Thus, the wastewater entered the reactor and the biomass discharge rate was at 0.2L/day. However, for HRT study, influent wastewater flow was adjusted according to their respective HRTs (Fig. 1).

900 cm^2 graphite electrode were submerged in anode and cathode side of the reactor and each electrode was connected by wires forming an electric circuit. A multimeter was attached to the electrical circuit to measure the voltage generated by the system. Anode and cathode chamber were separated by a baffle. Two peristaltic pump were set at the anode and cathode chamber to pump the wastewater into the reactor and transfer the treated wastewater for settlement before further analysis. Oxygen was supplied at the cathode chamber by using an air compressor meanwhile at the anode, magnetic stirrer was used to ensure no sludge sediment at the bottom of the reactor. For HRT study, HRT was controlled by adjusting the influent flow rate of the wastewater located at the anode compartment. Whereas for the MLSS study, the MLSS concentration of the operation was controlled by adjusting the concentration of the sludge. The range of HRT tested were 7 days, 8 days, and 9 days and the range of MLSS concentration tested were 1500 mg/L, 2000 mg/L and 2500 mg/L.

3. Results and discussion

3.1. The effects of HRT on COD and sulfide removal efficiency

The MFC performance in terms of wastewater treatment efficiency was studied by evaluating its COD and sulfide removal. The experiment were tested at three different HRTs of 7 days, 8 days and 9 days. Fig. 2 shows the COD and sulfide removal efficiency of MFC operation at different HRT.

Based on Fig. 2, it is shown that at HRT of 9 days, the MFC operation achieved the highest COD and sulfide removal efficiency of 98.24% and 98.98% respectively. The highest achievable COD and sulfide removal efficiency for HRT of 8 days were 89.18% and 97.99% respectively. Whereas, the highest achievable COD and sulfide removal efficiency for HRT of 7 days were 89.14% and 95.79% respectively. The result obtained from the present study demonstrated that the best operating HRT for the anoxic-aerobic MFC operated with spent caustic wastewater was at HRT of 9 days. Also from Fig. 2, despite the slightly fluctuated result of the removals, the trend of the COD and sulfide removal efficiencies at different HRT could still be observed in which higher HRT resulted in higher COD and sulfide removal efficiency. The result obtained is compatible with previous MFCs researches which reported that the COD removal efficiency is proportional to the HRTs. [51] conducted MFC operation with domestic wastewater as substrates reported that higher COD removal was due to longer HRTs [51]. Besides that, another research on wastewater treatment by using microbial electrolysis coupled with anaerobic digestion reactor operated with beer brewery wastewater reported that longer HRT was favourable for the operation of the reactor when maximum COD, TOC and carbohydrate removal efficiencies was achieved at the highest HRT of 36 h [52]. The same trend of COD removal efficiency with HRT was also observed by [53] whom conducted baffled stacking MFC operated with synthetic wastewater and Li et al. [54] whom conducted up flow tubular MFC operated with animal carcass wastewater [53,54]. The high COD removal efficiency achieved at high HRT was commonly explained in terms of the contact time between the compounds and microbes whereby higher HRT has allowed sufficient contact time for the microbes to maximize its pollutants removal efficiencies [54]. The same scenario had occurred in the present study in which the increase of COD and sulfide removal efficiency at higher HRT was due to longer time for wastewater to remain in the reactor allowing more substrates in the wastewater to be digested by the bacteria reducing its COD and sulfide concentration of the effluent wastewater. Luo et al. [55] stated that at higher HRT, sludge had longer residence time at the anaerobic segment and the organic matter in the sewage can be fully oxidized [55]. In terms of sulfide removal efficiency, it is observed that the MFC reactor in the present study was able to achieve high sulfide removal efficiency at every HRTs tested. The scenario was expected since sulfide also served as the key aspect in the electricity generation of MFC operation [56]. Sulfide is well known for redox shuttle between biocatalyst and insoluble electron acceptors and it also acts as electron carrier on the anode surface [57]. Therefore, sulfide removal efficiency was not only achieved by the presence of the well-functioning sulfur-oxidizing bacteria to degrade the sulfur content in the wastewater, but sulfide was also utilized for MFCs energy production. Thus, high sulfide removal could be achieved. It is reported that treatment of high strength wastewater generally required a longer HRT for effective nutrients and COD removal [16]. Isma et al. [40] also reported that high HRT is suitable for high concentration COD and BOD in wastewater [40]. Therefore, better removal efficiency of the anoxic-aerobic MFC at high HRT was expected as the system employed high strength spent caustic wastewater as the substrates.

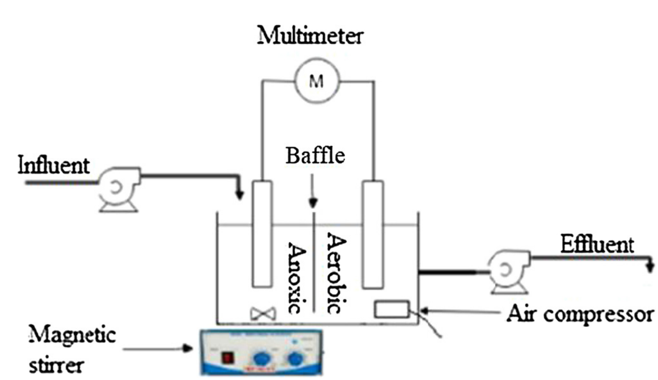

Fig. 1. MFC Setup.

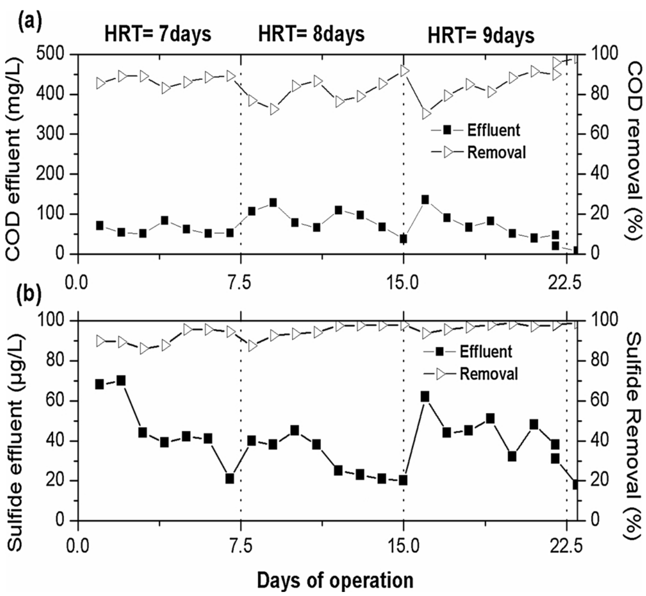

Fig. 2. a) COD effluent and COD removal at different HRT versus days of operation. b) Sulfide effluent and sulfide removal at different HRT versus days of operation.

HRT is also associated with the organic loading rate (OLR) of the system. It is often reported that the decrease in HRT could enhance the growth of microorganisms as low HRT resulted in higher F/M ratio in which would provide more nutrients to the biomass [40]. However, the MLVSS analysis conducted in the present study i.e. plotted in Fig. 3 shows that MLVSS is proportioned with HRT which indicates higher microorganism's concentration at high HRT. This could be due to the employment of spent caustic wastewater as substrates whereby spent caustic wastewater is readily available with sufficient nutrients for the biomass growth despite its higher HRT (lower OLR). Higher concentration of microorganisms in the system allowed higher pollutants degradation resulted in producing better quality effluent of spent caustic wastewater.

3.2. Effects of HRT on voltage production

The energy production of the MFC operation was measured in terms of its voltage generated in an open loop circuit. Fig. 4 shows the voltage production of MFC operation at different HRT.

From Fig. 4, it is shown that the highest voltage production of 81.2 mV was obtained at HRT of 9 days occur at day 16. However, the value decreased to the lowest voltage value of 26.4 mV occur at day 22.5. From the figure, it is also observed that each changes of HRT resulted in sudden increase in voltage production. Sudden increase in voltage production might be due to the existence of certain components in the spent caustic wastewater that are easily degraded by the bacteria, thus lead to increment in electron transfer rate. The same scenario encountered by Mansoorian et al. [58] whom conducted MFCs study with dairy industrial wastewater as the substrates reported that sudden increase in voltage may be due to the presence of chemicals in the wastewater which is easily used by the anode bacteria. After the substrates being used, the voltage gradually decreases [58]. However, the overall trend of the voltage production could still be observed and it is demonstrated that the voltage production was slightly higher at higher HRT. The result obtained in the present study is compatible with the previous MFC research by Liu et al. [42] employing domestic wastewater as substrates in which reported that power density increased when HRT was increased from 4.1 h to 11.3 h. The condition was explained in terms of the presence of the relatively high oxygen concentration in the cell that limits the generation of power density at low HRT [42]. Another MFCs research on animal carcass wastewater also reported the same trend of energy production with HRT and explained that the condition was due to longer contact time between the biofilm and organic material in wastewater which would benefits biofilms to uptake and degrade substrates, and to produce and transfer electrons onto the anode surface [59]. The same scenario had occurred in the present study whereby high HRT has provided enough contact time for the degradation of substrates in MFCs contributing to higher electron transfer rate and improves its energy production.

The result of the present study can be explained in terms of microbial population and activity as well. Based on the MLVSS analysis plotted in Fig. 3, it is shown that there was higher microorganisms' concentration which also indicates high microbial population in the system. The microbial population in the reactor consists of electrogenic and non-electrogenic microorganisms. According to Asensio et al. [60], the biomass of the reactor can be electrogenic but it can also include the non-electrogenic microorganisms and could be a completely non-electrogenic culture that may prevent the performance of the bioreactor as electrochemical cell [60]. Higher voltage production at higher HRT suggested that the MFC reactor was dominantly enriched with active electrogenic microorganisms contributing to better voltage production at higher HRT. High electrochemically active bacteria has resulted in increase of electron transfer efficiency in the MFCs reactor. According to Santos et al. [61] shorter HRTs diminished the cell voltage in accordance with the basic of the constancy of the microbiological population, the reduced electrochemical performance could be explained in terms of the more favourable development of non-electrogenic microorganisms moiety at larger OLRS (low HRT). In other words, higher HRT is favourable for the activity of the electrogenic microorganisms in terms of degrading large percentage of substrate and transforming it into electricity [61]. The present study has found that low HRT adversely affected the energy production of the MFC reactor in treating spent caustic wastewater. Previous research of MFC in treating refinery wastewater by Srikanth et al. [37] obtained result of similar trend with the present study in which sudden and significant increment in power output was observed immediately after increasing the HRT. The condition was reported to be due to the increase in contact time between the biocatalyst and refinery wastewater as the major reason behind the drastic increment in power output. MFCs operation at high HRT has supported the system for effective biocatalyst growth and electrogenic activity [37]. However, the present findings is also in contrast with a few MFC researches which reported that power density increased with decreasing HRT [62,55,63,42]. The improvement of MFC energy production at reduced HRT was commonly explained in terms of decrease

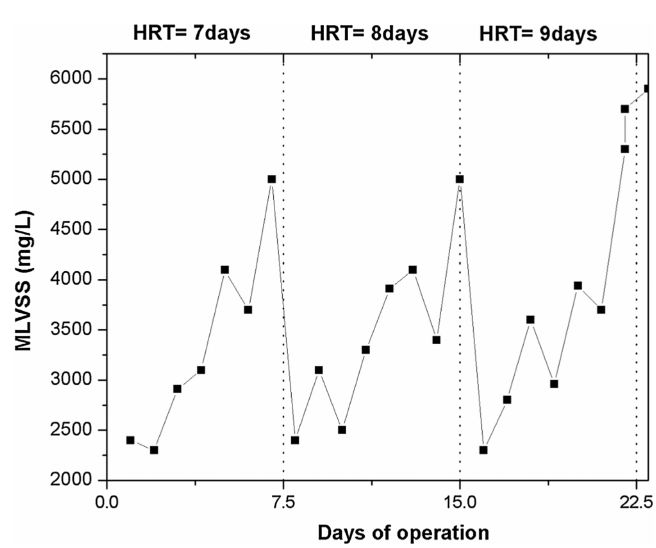

Fig. 3. a) MLVSS at different HRT versus days of operation.

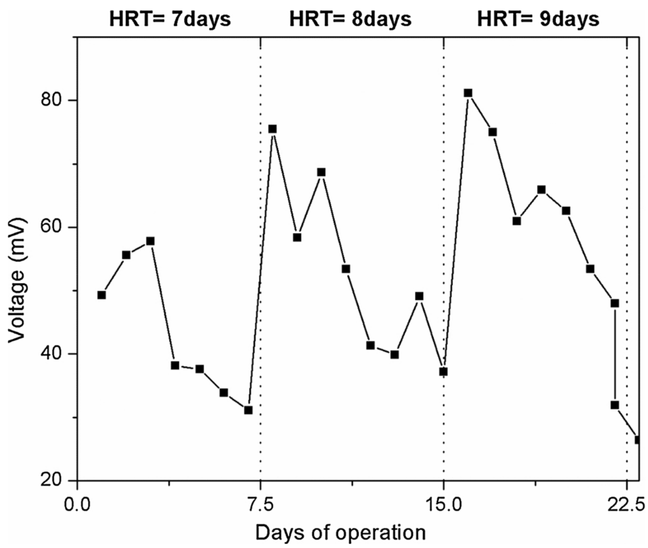

Fig. 4. Voltage generated at different HRT versus days of operation.

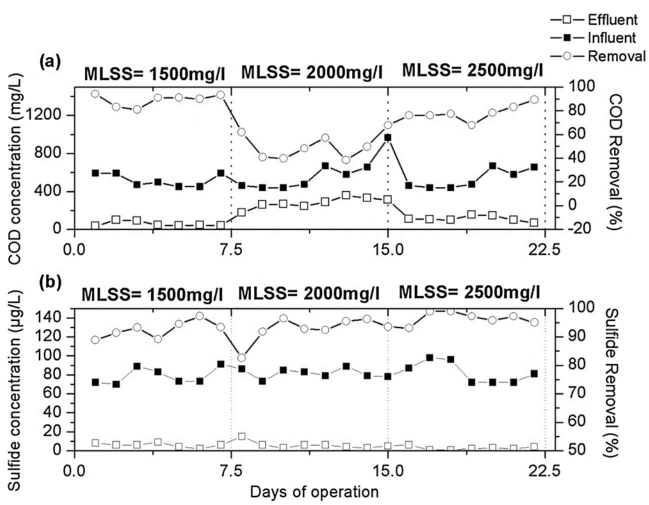

Fig. 5. a) COD effluent and COD removal at different MLSS versus days of operation. b) Sulfide effluent and sulfide removal at different MLSS versus days of operation.

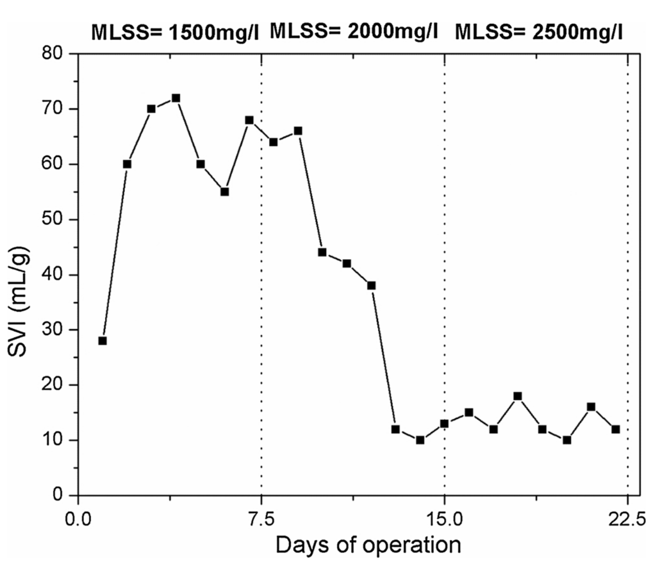

Fig. 6. SVI at different MLSS versus days of operation.

in substrate concentration and reduction in cell metabolism at high HRT [42]. HRT reduction has made the OLR increased correspondingly, lead to more decomposition of organic matter involved in the process of MFC power generation, thus promote to biomass to energy conversion [55].

3.3. Effects of MLSS concentration on COD and sulfide removal efficiency

The MFC performance in terms of wastewater treatment efficiency was also evaluated at different MLSS concentration of 1500 mg/L, 2000 mg/L and 2500 mg/L. Fig. 5 shows the MFC performance at different MLSS concentration.

From the figure, it is observed that COD and sulfide removal were fluctuated throughout days of operation. The highest COD removal efficiency was 94.07% achieved at MLSS of 1500 mg/L with 88.88% sulfide removal efficiency. However, the highest sulfide removal efficiency was 98.97% obtained at MLSS of 2500 mg/L with 76.14% of COD removal efficiency. Stable COD removal efficiency was obtained at MLSS of 1500 mg/L throughout day 5 to day 7. From the present study, it is demonstrated that the optimal performance of MFC in terms of wastewater treatment was achieved at lowest range of MLSS tested which is was 1500 mg/L. The result obtained in the present study is in contrast with previous researches which reported that increment in MLSS concentration resulted in better removal efficiency [64,44]. Zinadini et al. [44] conducted MFC integrated with membrane bioreactor operation operated with synthetic dairy wastewater explained that the increment of MLSS improved the organic removal efficiency as the high MLSS concentration in the anodic chamber lead to increase in substrate utilization and high COD removal efficiency [44]. However, in the present study, high removal efficiency achieved at low MLSS could be due to sufficient F/M ratio at low MLSS of 1500 mg/L. Increase in MLSS concentration led to low F/M ratio which indicates high biomass concentration within the system, resulted in overall population competition due to limited substrates concentration and reduced the organisms activity [45]. Besides that, at lower MLSS concentration, more specific surface area is available for the uptake of a substrate and enzymatic activity is higher in which could encourage faster waste degradation [64]. The optimal COD removal efficiency achieved at low MLSS concentration in the present study could also be explained in terms of the sludge characteristics i.e. sludge settleability. Fig. 6 shows the SVI analysis conducted to study the sludge behaviour of the MFC reactor at different MLSS concentration. From the figure, it is observed that low MLSS concentration resulted in good sludge settleability.

Based on Fig. 6, at MLSS concentration of 1500 mg/L, the SVI slightly fluctuated between 55 and 72 mL/g. The value of SVI at which below 80 mL/g portrayed at MLSS 1500 mg/L indicates good settling characteristics of the sludge. Good settling characteristics of the sludge prevents the biomass from being wash out from the system, therefore the biomass concentration can be maintained [65]. In the present study, despite at low MLSS concentration of 1500 mg/L, effective COD removal could still be achieved due to the amount of microorganisms present in the bioreactor was readily sufficient to degrade the organic matter in the spent caustic wastewater. As observed in Fig. 5, increasing the MLSS concentration deteriorates the COD removal efficiency. The SVI at MLSS of 2000 mg/L shows gradual decrease from 68 to 10 mL/g and the SVI value remained lower at MLSS 2500 mg/L. Too low in SVI value indicates rapid settling of sludge. This is unfavourable for the wastewater treatment process because it could cause turbid effluent as the sludge are weakly structured and small flocs [66]. Thus, the MFC system does not able to produce good quality effluent at an extremely low SVI encountered at high MLSS. The result obtained in the present study is compatible with some of previous researches which reported that COD removal could be efficiently removed at low MLSS concentration [67,45]. From the present study, it is agreed that MLSS concentration does affects the microorganism's activity and increasing the MLSS concentration does not improve the COD removal efficiency.

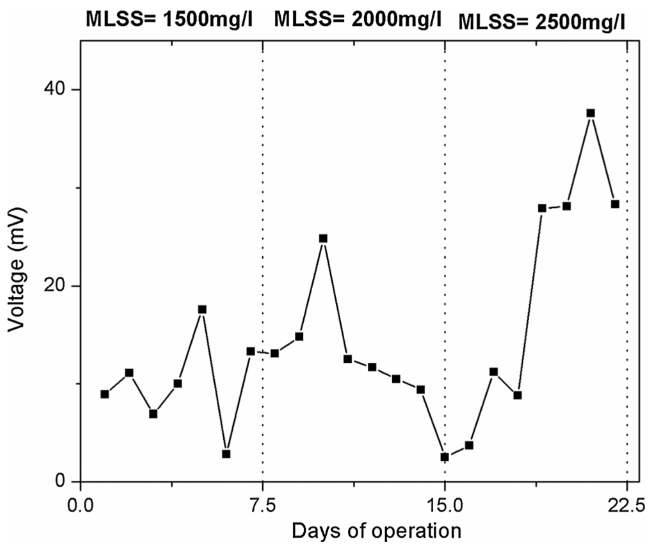

Fig. 7. Voltage generated at different HRT versus days of operation.

However, in contrast with the COD removal efficiency, sulfide removal efficiency was increased with increasing MLSS concentration. This result might be due to the presence of sulfur-oxidizing bacteria in the bioreactor that were functioning effectively and able to degrade the sulfur content in the influent wastewater. According to previous study of MFC employing sulfide as the substrates, it is reported that sulfide served as electron donor better than glucose for power generation of the mediator-less MFC system [68]. This means that sulfide does not only act as substrate for the microorganism degradation, but it also involved in the redox shuttle between biocatalyst and insoluble electron acceptor and act as electron donor [57]. In the present study, the highest voltage production of the MFCs occurred at MLSS of 2500 mg/L i.e. the highest range of MLSS tested. Also at this range, highest sulfide removal efficiency was 98.97% achieved. This shows that sulfide in the spent caustic wastewater was utilized for energy production of MFC, thus reducing its concentration in the effluent spent caustic wastewater.

3.4. Effects of MLSS concentration on voltage production

The energy production of the MFC system was investigated in terms of its voltage production operated in open loop circuit at different MLSS concentration and the result is shown in Fig. 7.

Based on Fig. 7, it is shown that the highest voltage of 37.6 mV was achieved at MLSS of 2500 mg/L whereas the lowest voltage recorded was 2.5 mV obtained at MLSS 2000 mg/L. The overall trend for voltage production of the MFC operation demonstrated that the voltage production increased with increasing MLSS concentration. The finding of the present study is in contrast with previous researches which reported that increasing MLSS concentration reduced the power generation of their respective system [44,46]. The condition was explained in terms of oxygen consumption by the electro-microorganisms. Oxygen served as electron acceptor in the MFC system thus its consumption by the electro-microorganisms is unfavourable as oxygen reduction would be reduced resulting in low energy recovery performance of MFC. According to Wang et al. [46], operating the MFC at relatively higher MLSS concentration could lower the impact of oxygen consumption by the electro-microorganism [46]. However, in the present study, the high voltage production occurred at high MLSS concentration was associated with the F/M ratio of the system. Increase in MLSS concentration has led to low F/M ratio and it is reported that low F/M ratio could improve the organic removal efficiency, sludge flocculation with an increased in power production [44]. Besides that, the high voltage production achieved at high MLSS concentration was also associated with the presence of higher sulfide-oxidizing microorganisms at high MLSS of 2500 mg/L. The presence of sulfide contaminants in the spent caustic wastewater was also the contributing factor to the high voltage production achieved as the highest sulfide removal efficiency was achieved at high MLSS of 2500 mg/L. This demonstrates that sulfide was well-utilized in the energy production of the MFC at high MLSS concentration of the system. Sulfide oxidation was reported to be the key aspect in electricity generation of MFC [56]. It is reported that sulfide is electrochemically active at the anode and is oxidized on the electrode surface, losses its electrons and is reduced to sulfate. This type of fuel cell has higher current density and does not require other heterogenous mediator as redox sulfide acts as mediator [58]. It is also observed that at high MLSS of 2500 mg/L, there was a formation of thick biofilm at the electrode surface. The same scenario was observed by [44] whereby at high concentrations of microorganisms, a thick biofilm was formed on the membrane surface and blocked the pores, thus caused the internal resistance to increase and lead to decreased in power generation. However, in the present study, the thick biofilm formation at the electrode surface does not block the transfer of electrons to the surface of electrode as it is reported that the bacteria attached could stimulates their nanowires to form bond between each other and provide electron transfer bridge [69]. Therefore, high voltage production could still be achieved despite of its high MLSS concentration.

4. Conclusion

The present study has demonstrated the capacity of MFC technology to produce an efficient wastewater treatment system that is energy benefits. The optimal HRT for the anoxic-aerobic MFCs operation operated with spent caustic wastewater was at HRT of 9 days as the highest COD and sulfide removal efficiency of 98% and 98.98% respectively were both achieved at HRT of 9 days. Higher HRT allowed longer retention time for microorganisms to oxidize the substrate. Highest voltage of 82.1 mV was also obtained at HRT of 9 days. At high HRT, the high microorganisms' concentration were dominantly made up of electrogenic bacteria causing high energy recovery of the MFC reactor at high HRT. Whereas for MLSS study, the optimal MLSS concentration for the MFC operation was 1500 mg/L with the highest COD removal of 94.07% and sulfide removal of 89.01%. High COD removal efficiency achieved at 1500 mg/L was due to sufficient F/M ratio at low MLSS at which the microorganisms' activity could be maintained as there was low population competition for substrates. However, sulfide removal efficiency was the highest at 2500 mg/L due to higher population of sulfur-oxidizing bacteria at high MLSS which also explained the highest voltage production at high MLSS as sulfide was well utilized for the energy recovery of the system. Thick biofilm formation was observed at the surface of electrodes at high MLSS without blocking the electron transfer to the surface of electrode as the bacteria attached could form electron transfer bridges. Thus, high voltage production could still be achieved despite the high MLSS concentration.

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