The Effect of COD Concentration Containing Leaves Litter, Canteen and Composite Waste to the Performance of Solid Phase Microbial Fuel Cell (SMFC)

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Abstract. This research is conducted to analyze and determine the optimum of COD concentration containing leaves litter, canteen and composite waste to power density and COD removal efficiency as the indicator of SMFC performance. COD as the one of organic matter parameters perform as substrate, nutrient and dominating the whole process of SMFC. Leaves litter and canteen based food waste were obtained from TPST UNDIP in Semarang and treated in SMFC reactor. Its reactor was designed 2 liter volume and equipped by homemade graphene electrodes that were utilized at the surface of organic waste as cathode and in a half of reactor height as anode. COD concentration was initially characterized and became variations of initial COD concentration. Waste volume was maintained 2/3 of volume of reactor. Bacteria sources as the important process factor in SMFC were obtained from river sediment which contain bacteroides and exoelectrogenic bacteria. Temperature and pH were not maintained while power density and COD concentration were periodically observed and measured during 44 days. The results showed that power density up to 4 mW/m^2 and COD removal efficiency performance up to 70% were reached by leaves litter, canteen and composite waste at days 11 up to days 44 days. Leaves litter contain 16,567 mg COD/l providing higher COD removal efficiency reached approximately 87.67%, more stable power density reached approximately 4.71 mW/m^2, and faster optimum time in the third day than canteen based food waste and composite waste. High COD removal efficiency has not yet resulted in high power density.

1 Introduction

SMFC has become an alternative technology of solid waste treatment converting solid phase material to eco-friendly product and directly electrical energy. In recent years, the application of SMFCs have attracted the highest attention on research although the value of current output from freshwater SMFCs was not higher than MFCs [1]. Various factors cover material type, size and volume, nutrient, water content, electrode type and configuration, design configuration, electricity circuit, pH, and temperature are affect the performance of SMFC. The problems were found where COD concentration containing material type affect the COD removal efficiency and electrical production. Buffiere et al. [2] stated that COD measurement is a very important to know the value of biodegradability from waste to produce energy. Output electrical power depend on complex organic type in waste which is hard degradable so it restrict electrical production [3]. High COD concentration means high COD removal efficiency and electrical production but it was the problem. Higher organic content, higher COD removal efficiency [4,5]. But many research found that high COD concentration was not necessarily producing high electricity [5-7. According to Song et al. [1] that he suggested the biomass addition with appropriate proportion could increase the contact opportunity between matrix (anode and the biomass addition), increase the organic waste content and increase the cellulose activities, then as an important method to increase power output in SMFCs. He also stated that due to high internal resistance and lower oxidation rate changes, where generally lower output power in SMFCs than MFCs, so SMFCs could be operated on higher external resistance to increase power output. Leaves litter, canteen and the composite of leaves litter-canteen have known containing high COD concentration that can be utilized as substrate in SMFC process. COD concentration is used as a main part of Dissolved Organic Matter (DOM) or Biological Oxygen Demand (BOD) that means organic biodegradable. High COD concentration means high DOM or BOD, removal efficiency, and electrical production. Because solid phase materials contain high COD concentration, the correlation of it is made to show the new observed contribution of high COD concentration in SMFC. The aim of this study is to analyze and determine the optimum of COD concentration containing leaves litter, canteen and composite waste to power density and COD

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removal efficiency as an indicator of SMFC performance.

2 Methods

Leaves litter, canteen and composite waste used in this study were collected from integrated solid waste treatment facility or it was called "TPST UNDIP" located on Diponegoro University in Indonesia. Waste samples were collected using Indonesia National Standard number 19-3964-1994 [8] about methods of sampling and measurement of generation and composition of urban waste. The collected wastes were identified as follows C-organic, N-Total, P-Total, C/N Ratio, pH, temperature, water content, and COD concentration using standard method analysis. River sediment as bacteria source were taken from Tanah Mas Semarang in Indonesia.

2.1. Reactor Design

SMFC has one compartment consists of catode and anode which were connected by electricity circuit and the distance between catode and anode is a half of reactor height. Its reactor was designed by 2 liter volume. Waste volume was maintained 2/3 of reactor volume along with water tap remaining to maintain moisture content and to enhance anolyte (substrate) conductivity [9]. del Campo [7] stated that 2/3 of waste volume was the optimum condition for metabolism bacteria. Sampling point was placed under the reactor which equipped by valve. Configuration of SMFC reactor is described in Figure 1 as follows:

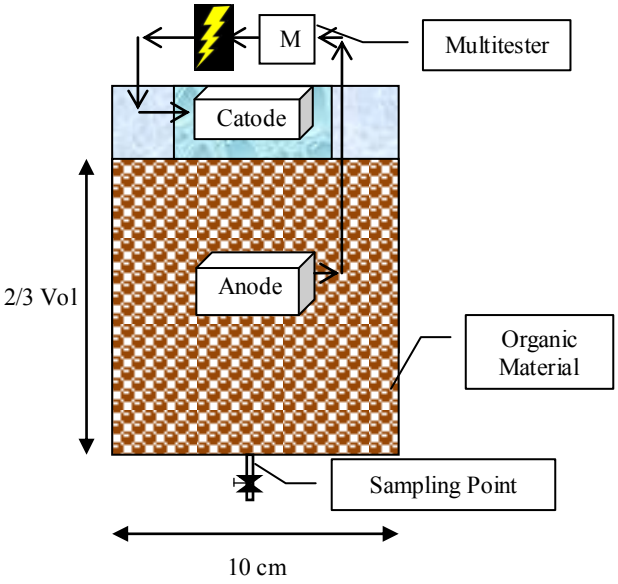

Fig. 1. SMFC Reactor Configuration.

2.2 Tools and Materials

The materials needed for this research consist of river sediment bacteria, chopped leaves litter 1.5 cm, fresh canteen based food waste, aquadest, mechanical pencil 2B, polyurethane, phosphate acid 85%, HCl 0.1 N, NaOH 0.1 N, wood glue, and sulphate acid 96% PA. The tools needed for this research consists of spectrophotometer, high digestion COD, low digestion COD, multimeter digital, pH meter, and thermometer.

2.3 Research Procedure

Research steps cover preparing step which were reactor construction and characterization test of leaves litter, canteen and composite waste, and also bacteria identification of river sediment that were used. Second step was main research which is started from seeding process to batch-running process. Its step was conducted during 44 days. At a certain period, sampling was conducted 15 times with the data taken cover COD in-out, voltage, ampere, resistance, pH, and temperature.
Research analysis covered COD removal efficiency and power density. In order to measure the COD, the samples were first diluted 10 times. Then 2 ml of the diluted samples were mixed with a digestion solution of a high-range COD reagent before heated at 150^{o}C for 2 h in a thermo reactor which was analyzed using a spectrophotometer. The performance of COD removal efficiency in SMFC was calculated by the COD removal using the following equation: $\eta = \frac{C_{inlet} - C_{outlet}}{C_{inlet}} x\ 100\%$; where η is the percentage of BOD and COD removal, C_{inlet} is initial BOD and COD concentration (mg/L) and C_{outlet} is BOD and COD concentration in certain of time. The power density was calculated using the following equation: P = I x R; where, R is the applied external resistance (ohm) and I is the current (amps). The current was measured using the following equation: I = V/R; where, I is the current (amps), V is the voltage (volt), and R is the applied external resistance (ohm) [10]. Approximation of power density formulation can be followed equation: $P = \frac{V\,x\,I}{A}$; where A (m^2) is surface area of graphene anode. The voltage was measured using a digital multimeter, and the power density curve was obtained.

3 Result and Discussion

Initial characteristics of leaves litter, canteen and composite waste showed that canteen waste has higher COD concentration than leaves litter and composite wastes. Food based waste generated from canteen operations has highly biodegradable solid waste [9]. The following is presented in Table 1.

Table 1. Initial Characteristics of Leaves Litter, Canteen and Composite waste.

Parameter	Unit	Value					
		LL		Cant.		Comp.	
C-Organic	%	49.46	48.40	71.60	46.11	89.61	16.90-19.60
N-Total	%	1.56	1.24	0.94	3.19	1.02	1.30
P-Total	%	0.02		0.01	10.40	0.01	
C/N Ratio		31.70	39.03	76.26	20-26	87.85	14-36.14
pH		6.30		7.37	6-6.5	7.37	6.0-8.0
Temperature	^{o}C	26.20		25.90		25.9	
Water Content	%	14.12	59.90	70.00	70.00	45.9	40.00-52.90
COD	mg/l	16,567		14,900	330,000-380,000	19,567	

Note: LL = Leaves Litter; Cant. = Canteen; Comp. = Composite

Based on the Table 1 that higher C-organic percentage and C/N ratio are not directly proportional with COD concentration. Water content affect COD concentration of all three materials which depend on C-organic percentage. Composite waste has particulary different result on COD concentration because of mixed materials between leaves litter and canteen waste. It can be said that higher C-organic percentage and C/N ratio with certain water content of composite waste provide different COD concentration result compared towards leaves litter and canteen waste. Because of this research based on an ideal condition so that the value of water content is avoided.

Only C-organic test result of two materials in accordance with the result of C-organic canteen waste reached above 46.11% [11], and C-organic composite waste reached in range 16.90-19.60% [12], except C-organic leaves litter test result reached below 48.4% [13]. N-Total and P-Total are not provide the same result that leaves litter reached 1.24%N-Total [13], canteen waste reached 3.19%N-Total and 10.4%P-Total [11], and composite waste reached 1.3%N-Total [12]. C/N ratio was also not provide the same result. pH and temperature are the physical standard parameter that were not significantly different or provide the same result. Water content of leaves litter result test was not provide the same result reached 59.90% [13], but water content of canteen and composite waste were provide the same result reached 70.00% [11,15] and reached 40.00-52.9% [12], respectively. COD concentration of canteen waste was only tested and reached 330,000-380,000 mg COD/l [14-15]. Meanwhile COD concentration of leaves litter and composite waste was not yet tested and experimented in SMFC.

Due to characterization of bacteria from natural river sediment is very important that become the main support on whole process of SMFC, then analysis of the existence of bacteria was obtained. The results were founded Escherichia coli as dominant and existence species in river sediment. The existence of bacteria in river sediment are identified in Proteobacteria phylum Escherichia, Salmonella, Desulfovibrio, Desulfobacteria, Acidovorax genus [16-19], Nitobacteria genus [20], and a half of Acidobacteria and Acinobacteria phylum [17], Nitrospirae phylum Nitrospira genus [17], Bacteroides phylum Flavobacterium genus [18], Firmicutes phylum Clostridium genus [19]. Proteobacteria phylum is a gram-negative type bacteria and facultative anaerobic which means that bacteria could live in available oxygen or not. This is accordance to running process on anaerobic SMFC. In the performance system of SMFC, Escherichia coli has a role to reduce glucose contained waste which was needed for reduction reaction with oxygen [21]. Proteobacteria phylum have the highest proportion to produce electricity [22]. According to research of Zhang et al. [23] that power density reached 100-600 mW/m^2 using Escherichia coli.

Mitov et al. [19] compared the performance of SMFC using river sediment and soil that river sediment showed the best performance of SMFC because of more organic substances and also the existence of exoelectrogenic bacteria with specific capability. Xing et al. [24] also stated that the river sediment has exoelectrogenic and fermentation function which known have good COD removal efficiency and electricity production.

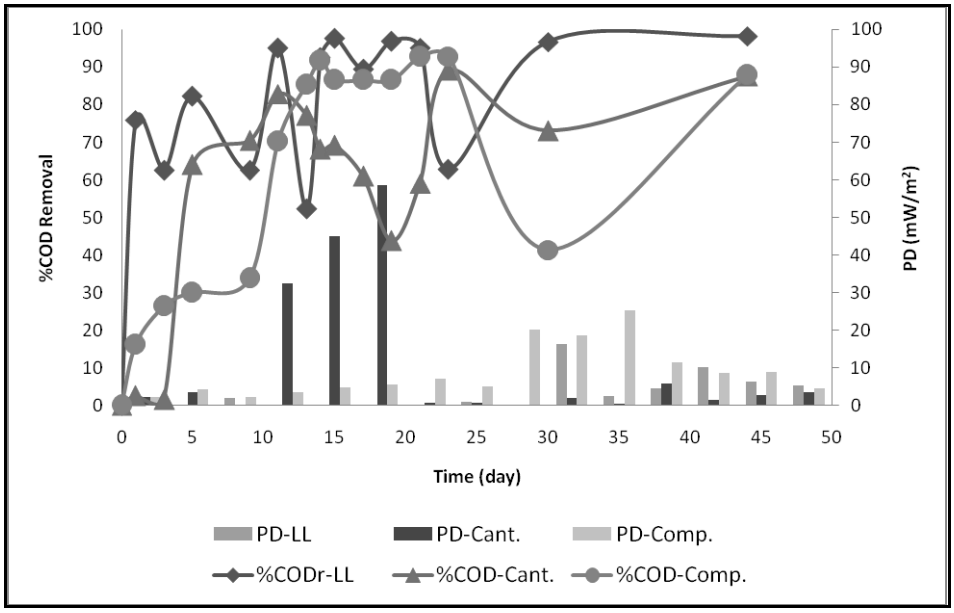

Fig. 2. Correlation of Waste Type to The Performance of SMFC.

An ideal condition that leaves litter, canteen and composite waste are adjusted by certain %C, %N-Total, %P-Total, C/N Ratio, pH, temperature, water content, and COD concentration provides the different results. Leaves litter contain 16,567 mg COD/l providing higher COD removal efficiency, more stable power density, and faster optimum time than 14,900 mg COD/l containing canteen based food waste and 19,567 mg COD/l containing composite waste as follows in Figure 2. Other reason is a statistical measure of how close the data are to the fitted regression or logarithmic or exponential line that means R-squared of percentage of COD efficiency, showed higher value of R-squared in canteen waste, composite waste and leaves litter, respectively. Based on scoring method, leaves litter also provide higher score than canteen and composite waste. Three statements based on the performance of SMFC result, R-squared, and the scoring method provide multiple argument, so the appropriate statement of leaves litter is selected as the optimum material. All of the statements can be stated that the optimum range of COD concentrations is 16,567 mg COD/l to 19,567 mg COD/l. This information opens up opportunities that the other of optimum range of COD concentration between 16,567 mg COD/l to 19,567 mg COD/l might be founded. Correlation of COD concentration with percentage COD removal efficiency and power density are described in Figure 3 as follows:

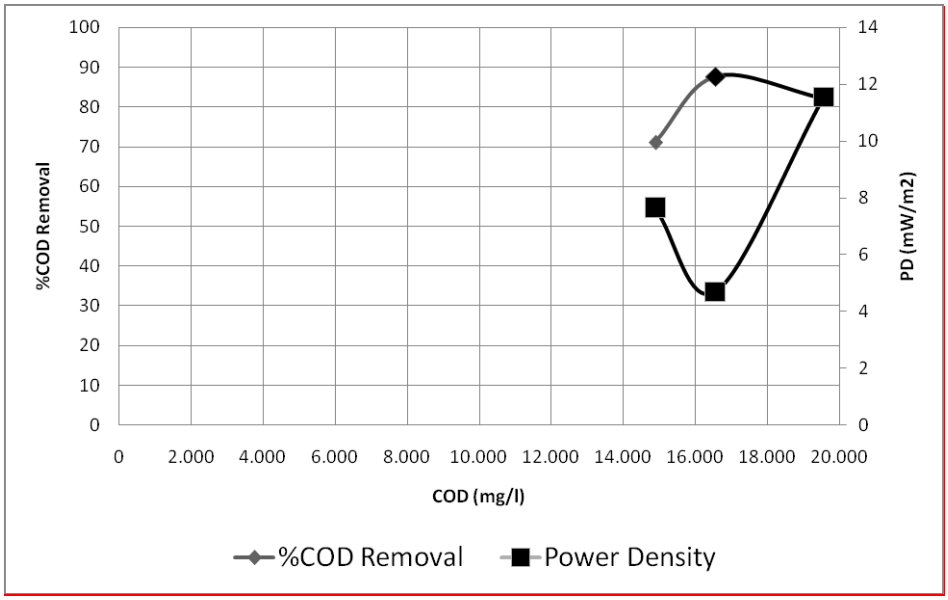

Fig. 3. Correlation of COD Concentration, COD Removal Efficiency and Power Density.

Correlation of COD concentration with percentage COD removal efficiency and power density are important that be high COD concentration has not yet high COD removal efficiency and power density. High COD concentration of 16,567 mg COD /l is an optimum COD concentration but power density performs lower value than low COD concentration of 14,900 mg COD /l and high COD concentration of 19,567 mg COD /l. It was same result with del Campo et al. [7] that the optimum result was not the highest COD concentration. It can be stated that high performance in COD removal efficiency has not yet resulted in high power density meanwhile

low COD concentration performs the stability of COD removal efficiency and power density. Based on the explanation above that COD concentration between 16,567 mg COD/l to 19,567 mg COD/l might be founded is reliable. The increasing of COD concentration from 16,567 mg COD/l to 19,567 mg COD/l could increased the power density, but the COD removal efficiency were not decreased significantly.

4 Conclusion

High COD removal efficiency has not yet resulted in high power density. The stability result showed in COD concentration of 16,567 mg COD/l. The increasing of COD concentration from 16,567 mg COD/l to 19,567 mg COD/l could increase the performance of SMFC. Leaves litter contain 16,567 mg COD/l mg COD/l providing higher COD removal efficiency, more stable power density, and faster optimum time than canteen based food waste and composite waste.

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