Correlation of COD and BOD of Domestic Wastewater with the Power Output of Bioreactor

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Summary: This research article deals with the studies on the development of the correlation of COD, BOD, and BOD_5 of domestic wastewater (DWW), and fermented domestic wastewater (FDWW) with the power output of the microbial fuel cell (MFC). The fermentation of DWW was carried out with yeast (*Saccharomyces cerevisiae*), and yogurt bacteria (*Streptococcus lactis*) to produce biohydrogen which was converted to the electrical energy through the development of microbial fuel cell (MFC). The values of COD, BOD, and BOD_5 for yogurt fermented domestic wastewater (Yogurt-FDWW) were found to be greater than the values of yeast fermented domestic wastewater (Yeast-FDWW). The power output of DWW and FDWW was increased with the increase in COD, BOD and BOD_5 values. The main objective of this article is to develop the renewable alternative of fossil fuels which are the major cause of global warming and global pollution.

Introduction

Presently, energy demands are fulfilled by different technologies including hydropower, fossil fuels, wind power, solar energy, nuclear energy *etc*. More than 80% of the total energy consumption worldwide is obtained by fossil fuels like petrol, diesel, gas, coal *etc*. Fossil fuels are non-renewable source of energy and they are the major cause of global warming and global pollution. Therefore, there is an urgent need to develop the environmental friendly alternative technologies for the efficient production of energy which can overcome the global energy crisis, global warming and global pollution. Electricity can be generated by using fermented domestic wastewater as well as carbohydrates and other biowastes [1-4]. Domestic wastewater is the cheapest source of energy which is composed of organic substrate like carbohydrates, proteins, fats, soaps, and detergents along with the presence of viruses, bacteria, and protozoa [5].

Chemical oxygen demand (COD) is a measure of the capacity of water to consume oxygen during the decomposition of organic matter present in a wastewater sample. COD measurements are commonly made on samples of wastewaters or of natural waters contaminated by domestic or industrial wastes. By COD determination it is possible to quantitatively evaluate organic and inorganic substances which can be oxidized by strong oxidants like $K_2Cr_2O_7$ in highly acidic solution. Standard dichromate method is often used to measure COD [6]. The value of COD is always higher than that of BOD because many organic substances can be oxidized chemically but can not be oxidized biologically. COD represents the total pollution load of the most wastewater discharges [7-9].

Biochemical oxygen demand (BOD) is the measure of the oxygen used by the microorganisms as they decompose the organic matter in the wastewater. It gives an indication of the amount of oxygen needed to biologically oxidize the organic matter present in a wastewater. The current international standard for measuring biodegradable organic levels in wastewater is the five-day biochemical oxygen demand (BOD_5) [10]. The test measures the quantity of dissolved oxygen (DO) consumed by microorganisms during the biological oxidation of organic matter under specified conditions. DO measurements can be conducted by the Winkler iodometric titration method [11, 12].

Microbial fuel cell is a device which can be used to convert the chemical energy into electrical energy through the fermentation of organic substrates by microorganisms [1, 2, 13, 14]. In microbial fuel cells, the fuel source is generally biodegradable organic matter. In general, there are two types of microbial fuel cells, namely mediator and mediator-less microbial fuel cells. A mediator-less microbial fuel cell does not require a mediator but uses electrochemically active bacteria to transfer electrons

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to the electrode [1, 2, 14]. Among the electrochemically active bacteria are *Shewanella putrefaciens*, *Aeromonas hydrophila* and others [1, 2, 15]. Most of the microbial cells are electrochemically inactive. Therefore, the electrons transfer rate from microbial cells to the electrode is facilitated by using the mediators such as thionine, methyl viologen, methyl blue, humic acid, neutral red *etc*. [16].

Results and Discussion

Physical Parameters

pH of the fermented domestic wastewater (FDWW) sample was found to be lower than distilled water (DW), and domestic wastewater (DWW), and its range was found to be 6.4 to 7.2. The decrease in pH showed that the acid strength of FDWW is increased due to the formation of acids by bacterial biodegradation of the organic matter. The acid strength of DW, DWW, Yeast-FDWW (0.5 and 1.0 g), and Yogurt-FDWW (0.5 and 1.0 g) was found to be 0.001, 0.013, 0.017 (0.5 g), 0.020 (1.0 g), 0.036 (0.5 g), and 0.047 M (1.0 g), respectively. The range of the conductance was found to be 30 to 729 µS/cm. There was an increase in the conductance of FDWW as compared to DW and DWW. It is because of the formation of the new electrolytes due to the metabolic activities of the microorganisms. The range of the absorbance was found to be 2.081 to 2.271 at 331 nm wave length. There was an increase in the absorbance and decrease in the transmittance of the FDWW as compared to DW and DWW (Table-1).

The values of COD for DW, DWW, Yeast-FDWW (0.5 and 1.0 g), and Yogurt-FDWW (0.5 and 1.0 g) were found to be 0.00, 113.40, 127.58 (0.5 g), 354.81 (1.0 g), 155.93 (0.5 g), and 367.48 mg/L (1.0 g), respectively. Similarly, the values of BOD for samples mentioned as above were found to be 0.00, 1.2, 2.3 (0.5 g), 3.5 (1.0 g), 3.6 (0.5 g), and 4.0 mg/L (1.0 g), respectively. In addition, BOD_5 for these samples were found to be 1.4, 2.2, 3.0 (0.5 g), 3.1 (1.0 g), 3.3 (0.5 g), and 3.4 mg/L (1.0 g), respectively. It showed that greater the strength of the organic compounds more will be the COD and BOD of wastewater. The values of power output (mW) were found to be 0.35 (DWW), 0.48 (Yeast-FDWW, 0.5 g), 0.51 (Yeast-FDWW, 1.0 g), 0.54 (Yogurt-FDWW, 0.5 g), and 0.61 mW (Yogurt-FDWW, 1.0 g) (Table-2).

Correlation of COD and BOD with the Power Output

COD and BOD are referred to as wastewater quality indicators. Therefore, by measuring the COD and BOD values of the wastewater samples the strength of the chemical compounds can be easily measured. The strength of the chemical composition of wastewater is directly proportional to the concentration of the biohydrogen production. Greater the strength of the organic matter of wastewater more will be the biohydrogen and more will be the power output of the bioreactor. All the experiments and observations showed that the values of COD, BOD, and BOD_5 are directly proportional to the power output of the bioreactor. Hence, the strength, nature and composition of the organic matter present in the wastewater can directly effect on the power output of the bioreactor. The water samples which have high COD, BOD, and BOD_5 values have greater tendency for biopower generation. Yeast-FDWW and Yogurt-FDWW showed high COD, BOD, and BOD_5 values as compared to DWW. Furthermore, Yogurt-FDWW showed high COD, BOD, and BOD_5 values as compared to Yeast-FDWW (Table-2).

Table-1: Physical parameters of water samples.

Sample codes	pH	Acid strength (moles/dm^3)	Conductance (µS/cm)	Absorbance* (A)	Transmittance (%)
DW	**7.0**	**0.001**	**30**	**0.000**	**100**
DWW	**7.2**	**0.013**	**681**	**2.081**	**0.829**
Yeast-FDWW (0.5 g)	**6.8**	**0.017**	**696**	**2.214**	**0.610**
Yeast-FDWW (1.0 g)	**6.7**	**0.020**	**703**	**2.271**	**0.535**
Yogurt-FDWW (0.5 g)	**6.5**	**0.036**	**705**	**2.226**	**0.594**
Yogurt-FDWW (1.0 g)	**6.4**	**0.047**	**729**	**2.171**	**0.674**

* Wave length (λ) for absorbance = 331 nm.

Table-2: Comparative data of different water samples.

Samples codes	COD (mg/L)	DO initial (mg/L)	DO final (mg/L)	BOD (mg/L)	BOD_5 (mg/L)	Current (mA)	Voltage (mV)	Power P = VI (mW)	Resistance (Ω)
DW	**0.00**	**7.6**	**6.2**	**0.00**	**1.4**	**-**	**-**	**-**	**-**
DWW	**113.4**	**6.4**	**4.2**	**1.2**	**2.2**	**0.23**	**1.5**	**0.35**	**6.521**
Yeast-FDWW (0.5 g)	**127.58**	**5.3**	**2.3**	**2.3**	**3.0**	**0.3**	**1.6**	**0.48**	**5.333**
Yeast-FDWW (1.0 g)	**354.81**	**4.1**	**1.0**	**3.5**	**3.1**	**0.32**	**1.6**	**0.51**	**5.0**
Yogurt-FDWW (0.5 g)	**155.93**	**4.0**	**0.7**	**3.6**	**3.3**	**0.34**	**1.6**	**0.54**	**4.70**
Yogurt-FDWW (1.0 g)	**367.48**	**3.6**	**0.2**	**4.0**	**3.4**	**0.36**	**1.7**	**0.61**	**4.72**

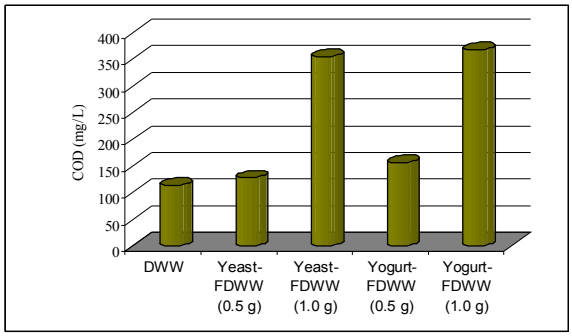


Fig. 1: Comparison of COD values for different water samples.

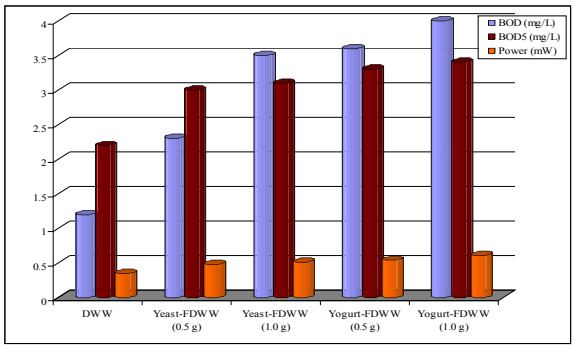


Fig. 2: Comparison of BOD, BOD_5 and power output for different water samples.

Experimental

Collection and Fermentation of Domestic Wastewater (DWW)

About 20 liters of DWW sample was collected from the main sewage line located near Mausamiyat, Karachi, Pakistan. This sewage line is coming from the residential area of Mausamiyat near University of Karachi. The wastewater sample was filtered by cotton cloth for removing the solid particles. Fermentation of DWW was carried out by adding yeast (0.5 and 1.0 g), and yogurt (0.5 and 1.0 g) separately into 300 mL DWW and then incubated at 37 °C for 24 hours and five days (Scheme-1).

Standardization of Ferrous Ammonium Sulphate (FAS)

Ferrous ammonium sulphate (FAS) is a secondary standard solution which was standardized by $K_2Cr_2O_7$ (0.25 N). The FAS solution was prepared by taking FAS (39 g) in 1000 mL volumetric flask and dissolved it by adding distilled water and make up the volume up to the mark. For standardization, 5 mL standard $K_2Cr_2O_7$ (0.25 N) solution and 50 mL distilled water were taken in conical flask, 15 mL H_2SO_4 was slowly added and the reaction was cooled at room temperature. Ferroin Indicator (2-3 drops) was added and the reaction mixture was titrated with FAS, the color was changed from yellowish orange to bluish green which was the end point of reaction. Normality of FAS was calculated by the relation:

$$\text{Normality of FAS} = \frac{(\text{Vol. of } K_2Cr_2O_7)(\text{Normality of } K_2Cr_2O_7)}{\text{Vol. of FAS required}}$$

$$\text{Normality of FAS} = \frac{5 \times 0.25}{4.1}$$

$$\text{Normality of FAS} = 0.088 \text{ N}$$

Procedure for COD

The COD of DWW and FDWW was determined by dichromate standard reflux method [6]. For the determination of COD different solutions were prepared and standardized by titration method. Now 25 mL blank solution (distilled water or wastewater), $HgSO_4$ (0.5 g), H_2SO_4 (2.5 mL), and $AgSO_4$ (1.0 g) were taken in 500 mL refluxing flask and then mixed until the solution was cleared. Now, 12.5 mL of $K_2Cr_2O_7$ (0.25 N) was added in the reaction mixture and mixed thoroughly. While mixing, H_2SO_4 (35 mL), and $AgSO_4$ (1.0 g) were added. The flask was connected to the reflux condenser and refluxed the reaction mixture by using stirring hot plate for 1 hour. Reaction mixture was allowed to cool down at room temperature (32 °C), and interior surface of the condenser and flask was washed twice with approximately 12.5 mL distilled water. The reaction mixture was diluted with approximately 175 mL distilled water followed by the addition of Ferroin Indicator (5-6 drops). The reaction flask was placed on a magnetic stirrer and titrated with FAS (0.088 N) with continuous stirring until the light green color, then dark green, bluish green and again light green color was appeared. Color was finally changed to reddish brown by the addition of last one drop of FAS which was recorded as the end point of the titration.

COD of different samples was calculated by the relation:

$$\text{COD (mg/L)} = \frac{(8000)(b - s)\,N}{\text{Sample volume (mL)}},$$

where:

8000 = Milliequivalent weight of oxygen x 1000 (mL/L)

b = Vol. of FAS used for blank (DW)
s = Vol. of FAS used for sample (DWW or FDWW)
N = Normality of FAS

Preparation of Sodium Thiosulphate Solution

Sodium thiosulphate (0.025 M) was prepared in 500 mL volumetric flask. The amount of sodium thiosulphate was determined by the relation.

$$\text{Amount} = \frac{\text{Molarity x molecular weight x volume}}{1000}$$

$$\text{Amount} = \frac{0.025 \times 248 \times 500}{1000}$$

Amount = 3.1g/500 mL

Now sodium thiosulphate (3.1 g) was taken in 500 mL volumetric flask and dissolved it by adding the distilled water, and finally make up the volume upto the mark. For the preservation of the solution, NaOH (0.2 g) was added into the volumetric flask.

Preparation of Alkaline Iodine Solution

For the preparation of alkaline iodine solution, NaOH (25 g), and KI (7.5 g) were dissolved in distilled water and then diluted upto 50 mL.

Preparation of Starch Indicator

For the preparation of starch indicator, starch (2 g), and salicylic acid (0.2 g) were dissolved in 100 mL boiling water and then the mixture was cooled at room temperature. Salicylic acid was used for the preservation of starch indicator.

Preparation of Manganese Sulphate Solution

For the preparation of manganese sulfate solution, manganese sulfate (20 g) was dissolved in 100 mL distilled water and subjected to the filtration.

BOD by Winkler Method

BOD of wastewater was determined by the difference of DO values of DW and wastewater samples while biochemical oxygen demand for five-days (BOD_5) can be determined by the difference of DO of two wastewater samples (one sample was incubated for 24 hours and another sample was incubated for five days at 37 °C) collected from the same source. The DO concentration level was determined by Winkler Method [11, 12]. First of all 300 mL of DW, DWW, and FDWW were separately taken in BOD bottles. In order to remove the air, the stopper was inserted on BOD bottle in such a way that the extra sample should be removed from the bottle. Manganese sulfate solution (1.0 mL), and alkaline iodine solution (1.0 mL) were added into the BOD bottle then stopper was inserted in the bottle. After shaking, H_2SO_4 (1.0 mL) was added and mixed it well which resulted in the dark brown color of the reaction mixture. This reaction mixture was titrated with sodium thiosulfate solution (0.025 M) until the solution was turned to pale yellow that was turned to blue color by the addition of starch solution (2.0 mL). Titration was continued until the color was permanently disappeared which gave the volume of sodium thiosulphate. To determine the BOD_5 values, all the samples were incubated for five-days at 37 °C before the performance of Winkler Method.

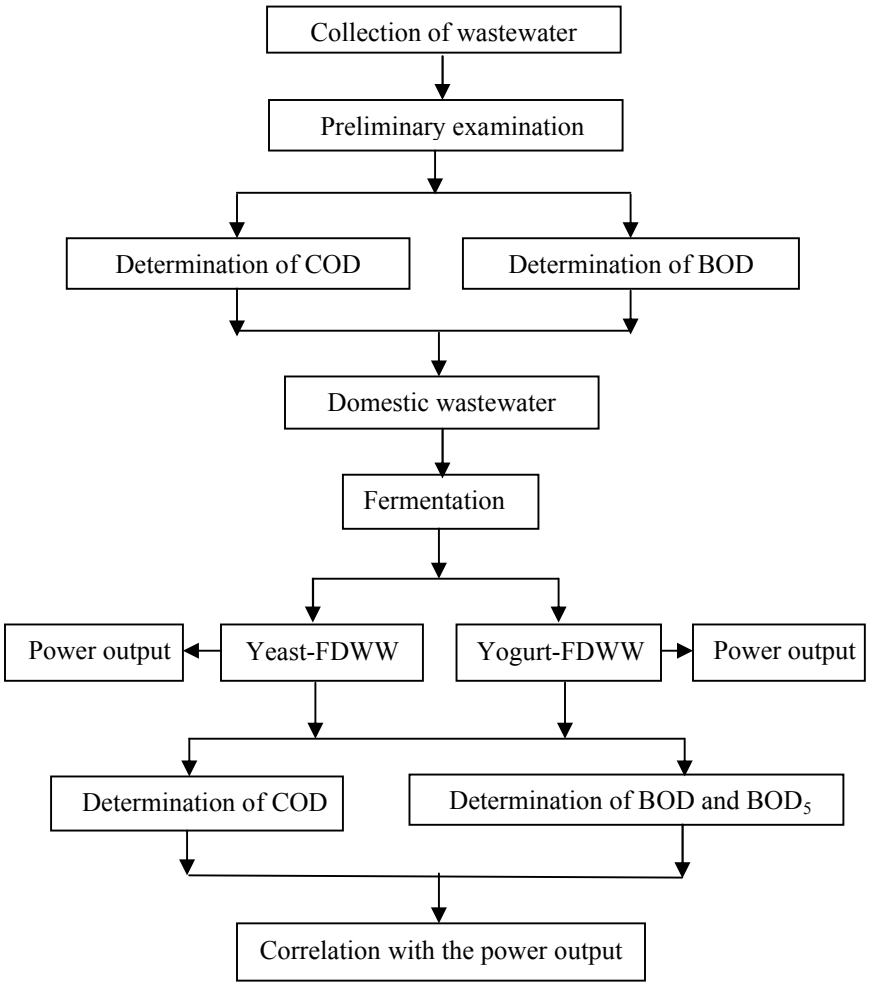
BOD_5 was calculated by the relation:
BOD_5 = DO initial – DO final
DO initial = Dissolved oxygen level for 24 hours incubation.
DO final = Dissolved oxygen level for five days incubation.

Construction of Microbial Fuel Cell

In order to determine the current and voltage of DWW and FDWW, double chamber open system microbial fuel cells (DCOS-MFC) were constructed using the two plastic chambers of two liters capacity, connected with sand-salt bridge (S_2-bridge) [1]. The salt bridge was prepared by using sand (5.0 g), and sodium chloride salt (100 g). DWW (2 liters), and FDWW (2 liters) were separately taken in anodic chamber containing Zn plate as anode. Distilled water (2 liters) was taken in cathodic chamber containing Cu plate as cathode (Fig. 3). The terminals of both electrodes were connected with the multi-meter (SANWA, MM, CD771, China). Current and voltage were recorded after the intervals of 24 hours (Scheme-1). Resistance (Ω), and power output (mW) of DWW and FDWW were determined by the relations R = V/ I and P = VI respectively.



Fig. 3: Determination of current and voltage of DWW.



Scheme 1: Experimental pathway for the determination of COD, BOD, and BOD_5 of wastewater samples.

Conclusions

The acid strength of FDWW samples was increased due to the process of fermentation. The values of conductance were also increased for FDWW samples as compared to the DWW samples which showed that the fermentation resulted in the increase of electrolytes in the reaction mixture. Power output was observed to a significant level by using the S_2-bridge. The purpose of these experiments is to compare the values of COD, BOD, and BOD_5 of wastewater samples (DWW and FDWW) with the power output of the microbial fuel cell (MFC). On the basis of these results it was concluded that the values of COD, BOD, and BOD_5 has a direct effect on the biohydrogen production and their values are directly proportional to the power output of the bioreactor. In addition, the outcome of this research will be helpful to develop the area of green energy and to overcome the energy crisis, global warming and global pollution.

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