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Generation of Electricity from Whey: An Electrochemical Process

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Abstract- This study is concentrated on the electricity generation from whey over and done with a fabricated electrochemical cell. Whey (milk serum) is one of the prominent sources of bio-electrolyte because of containing abundant amount of branched-chain amino acids. It is one of the non-useable by-products in the sweetmeat company and also harmful for our environmental pollution in case of open dumping. We choose whey because of its low pH content about 3.1-3.3. Moreover, the utilization of this kind of waste material can be important raw materials for power generation. Two categories of preservation techniques have been revealed by thermal treatment and adding 2% phenol by volume. It was observed that phenol treated whey was free form microbial attack for longer time compared to that of thermal treatment. The measurement of voltage and power density is important to estimate the efficiency and competency of the system. In agitation assisted bio-electrochemical reactor, voltage and power density were increased with the increase of electrode surface area. Maximum 17.35 volt was obtained from 6.5 litres of whey through an agitation assisted electrochemical reactor. In addition, commercial alloy electrode shows satisfactory results on power generation and reducing internal resistance compares with the experimental pure metal electrode. This technology has implication on the recovery of the power crisis in rural and remote areas where the national electricity supply is inaccessible. This approach is also convenient for portable use of electricity in household purposes.

Keywords Bio-electricity, Whey, Bio-electrochemical reactor, Amino acid, Baffle agitation system

1. Introduction

The future electricity generation will be certainly included with the most promising systems, which must have great attention by virtue of their inherently ultra-clean, efficient, and reliable performance. All over the world, biomass-to-electricity generation has gained importance due to the reduction in reliance on fossil fuels and positive environmental benefits. Bio-electricity is a new term in the field of bio-energy. The technology of bio-electricity generation in forms of fuel cell is a microbial fuel cell. In a microbial fuel cell, wastewater is managed by microorganism to generate fuel [1-3] such as ethanol, methane and hydrogen from organic matter, and these cells are designed with anode and cathode, separated by a membrane. These fuel cells are applied where dual activity could significantly reduce the cost associated with the electricity generation and wastewater treatment methods [4-8]. It produces very low power electricity. Fuel cell stack design with these methods is very complicated. Suitable substrate for microorganism in wastewater is not always available. This method is applicable for dual activity, such as wastewater treatment and small scale electricity production, and major purpose sits on wastewater treatment. Fortunately not having these kinds of limitations, our newly proposed bio-electrochemical cell also has ability to convert chemical energy directly into electricity without the combustion process. Moreover, the design and mechanism of electricity production in microbial fuel cell technologies are totally different from our proposed technology. Such a distinctive electricity generation by bio-electrochemical process could be a fast substituting reciprocating engines and gas turbines as the most environmentally-friendly sources of on-site power due to its low cost investment. In this study, the new approach of electricity generation prefers a distinct source of electrolyte with a novel fabricated electrochemical cell design.

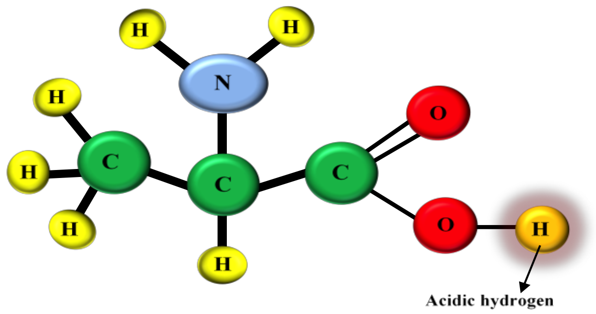

Fig. 1. A general structure of amino acids with highlighted acidic hydrogen

Organic acid like amino acid (Fig. 1) acts as a principle component of electrolyte in this electrochemical cell. Whey is one of the pronounced sources of the amino acid. It is a by-product found during the making of cheese or casein in foods and Sweetmeat Company. The supply of whey can be available around the year, and there is no use of it. This is mainly a waste product from the dairy farms. As a result, whey is totally thrown away into the drain (open dumping) by the sweet meat companies, and it causes environmental water pollution by microbial attack. In this study, whey is collected from the food industries in Sylhet city, Bangladesh. Most of the food industries (mainly sweet meat companies) use milk to produce their product and drainage the whey as a waste. The total amount of whey produced in Sylhet city is about 20,000 litres per day according to our survey. Therefore, it is expected that a huge amount of waste whey can be collected from throughout the country to the purpose of electricity generation. Moreover, it is a dilute solution of protein, lactose, fat and ash. Protein consists of long chain amino acid. According to equation (1), weak organic acid of electrolyte dissociates in aqueous solution, consequently hydrogen ions (H^+) are increased due to increase hydrophilic nature of amino groups and carboxylic groups [9]. Meantime, Zinc (Zn) plate dissolved in the organic electrolyte as Zn^{2+} ion sacrificing two electrons as shown in equation (3). Equation (2) shows that electrons from Zn plate passes through the external circuit, and salt of Zn is produced. On the other hand, in equation (4), H^+ ions are adsorbed on the surface of Copper (Cu) plate and receiving electrons, they evaluated as hydrogen gas (H_2).

$$H_2N-CHR-COOH\ (aq.) \rightarrow H_2N-CHR-COO^- + H^+ \quad (1)$$

$$2(H_2N-CHR-COO^-) + Zn^{2+} \rightarrow (H_2N-CHR-COO)_2Zn \quad (2)$$

At anode:

$$Zn\ (s) \rightarrow Zn^{2+}\ (aq.) + 2e^- \quad (3)$$

At cathode:

$$2H^+\ (aq.) + 2e^- \rightarrow H_2\ (g) \quad (4)$$

This approach is fully environmentally friendly because of its nil carbon dioxide emission. If the emission of hydrogen gas is captured, it must be one possible source of hydrogen fuel in large-scale electricity generation. Long term and unrestricted dumping of raw whey can cause fatal water pollution [10]. In most of the cases, sweetmeat companies in Bangladesh are used to do this bad practice. Consequently, high biological oxygen demand (BOD) in raw whey, about 40,000–60,000 ppm, interrupts the biological progressions of sewage treatment plants [11, 12]. In this bio-fuel cell, the raw whey was used to generate bio-electricity by several treatment processes to reduce the microbial growth. The effect of electrode surface area on power density and internal resistance was studied to increase the electricity generation. Development of preservation technique and fabrication of novel agitation assisted electrochemical cell reveal the new avenue for electricity generation.

2. Material and Methods

2.1. Electrolyte Selection and Processing

Several sources were studied as a bio-electrolyte and selected because of some properties like low pH, high electrical conductivity, economic value and availability.

Moreover, the sources are easily available and inexpensive bio-extracts such as tomato juice, tamarind juice and milk whey. Here, the study is mainly focused on milk whey (Fig. 2(A)). Among them, milk whey shows its reasonable performance to generate electricity based on its availability, pH, electrical conductivity and environmental impact. Two pre-treatment processes were applied to preserve the fresh bio-electrolyte (whey), highlighted in Table-1. Here, antibacterial reagent (2% phenol by volume) is subjected to bio-electrolyte for the preservation. Moreover, phenol is water soluble weak acid, which is freely absorbed by microorganisms when sufficient mineral nutrients are present in the soil. Enzymes or selection of organisms are used to degrade individual phenolic acids [13]. Therefore, there is no significant adverse impact on the soil when exhausted phenolic bio-electrolyte (whey) is discharged after electricity generation [14]. Thermal treatment at 70 °C about 5-7 minutes is another way to preserve bio-electrolyte, but it was observed that thermal treatment saves bio-electrolyte from microbial attack for less than two days. On the other hand, 2% phenol by volume represents more effectual to preserve the bio-electrolyte for more than four days.

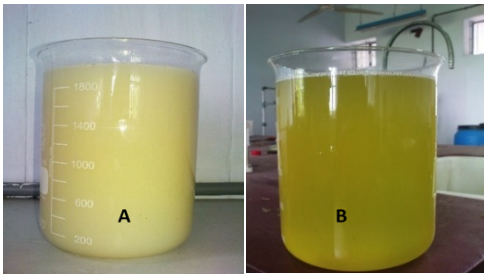

Fig. 2. (A) Electrolyte with 2% phenolic treatment before experiment and (B) exhausted electrolyte after experiment

Table 1. Preservation techniques of electrolyte.

No.	Types of process	Procedure
I	Preserving whey with antibacterial reagent	By adding 2% phenol
II	Preserving whey with thermal treatment	Thermal treatment at 70 °C about 5-7 minute (without adding any antimicrobial reagent)

2.2. Bio-electrochemical Cell Design and Measurement

This study is based on the continuous mode electricity generation through a bio-electrochemical reactor. The proposed bio-electrochemical reactor was consisting of several components such as the cell boxes or container, electrodes, separators, plastic pipes, pump circulating electrolyte, wood stand and connecting wire. The basic reactor design is based on the simple electrochemical cell, but a simple modification is added in a novel proposed reactor for amplification of its electricity generation capability. The cells were designed and connected in this reactor as depicted in Fig. 3. A design was fabricated by wood frame and four empty battery cases (cell containers) of 16 cells. A diaphragm pump (TYP-2000) was used for bio-electrolyte handling continuously, and cell boxes were connected with plastic pipes for the circulation of bio-electrolyte. The bold spiral path shows the movement of electrolyte within the cell box. This is called baffle agitation system. This type of flow pattern prevents the formation of dead zones and distributes the bio-electrolyte evenly throughout the cell boxes. Moreover, to reduce the internal resistance and total suspended solid into the electrolyte, the baffle flow agitation system had a great influence on this experiment. About 6.5 liters of whey is loaded in this baffle agitation system and circulated continuously for a 24 hours of operation.

To prepare cost effective bio-electrochemical reactor, empty battery boxes (containers) were collected from local market. After washing the boxes, electrodes of copper and zinc having dimensions of height: 10.8 cm, length: 5.4 cm and weight: 12 gm were inserted with whey into the containers. A container of four compartments has been shown in Fig. 4, where each compartment holds following dimensions - width: 4 cm, length: 8.4 cm, height: 10.5 cm, and effective height of the electrolyte: 9.5 cm. For achieving high voltage and high current yield, combinations of series and connection have been applied within the anode and cathode of this novel bio-electrochemical reactor. The generation of electricity to be continued until the anode plate gets totally corroded [15]. A meaningful arrangement of electrode (2:1 anodes-cathode ratio) is added to generate the maximum yield by increasing the anodic surface area. Polymeric separator is chemically stable to the electrolyte that has been used in between anode and cathode.

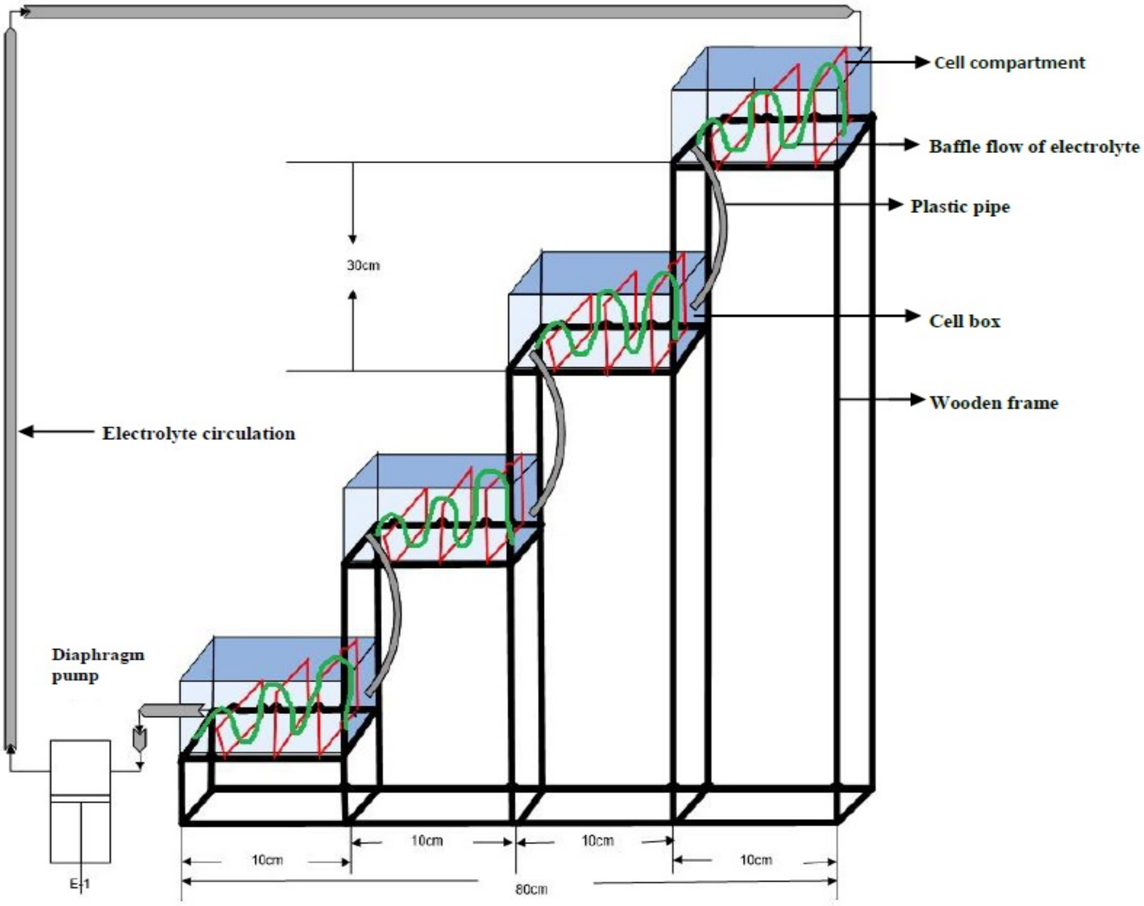

Fig. 3. Design of bio-electrochemical cell with baffle agitation system

It was also observed that commercial electrodes (CEs) showed better performance than pure metal experimental electrodes (EEs) such as pure Zn and Cu electrodes for producing more voltage and decreasing internal resistance. CEs are fabricated by mixing of different metals in different proportions which are highly potential for electrochemical cell. To observe the effectiveness of commercial electrodes, the experiment was run with single cell container (Fig. 4) of containing 2:1 anode-cathode system. A batch of 1.25 liters of phenolic treated whey was operated with both experimental electrodes and commercial electrodes for 15 hours.

A digital multi meter (FLUKE-87-V) was used to measure current (I), voltage (V) and emf (E). The outputs were recorded on hourly basis with the connection of 50 Ω (ohms) resistor as an external circuit. Power (P) in watt (W) was calculated using the equation P = IV, where I and V were measured in amperes and volts, respectively. Power density (W/ m^3) was computed according to Fan and his co-authors [16]. All experiments have been accomplished repeatedly minimum three times, and taken average value of the operating variables such as voltage, current, pH change and internal resistance. Table 2 illustrates the accuracy and maximum operating range of multi-meter, pH meter and conductivity meter that were used during the measurements.

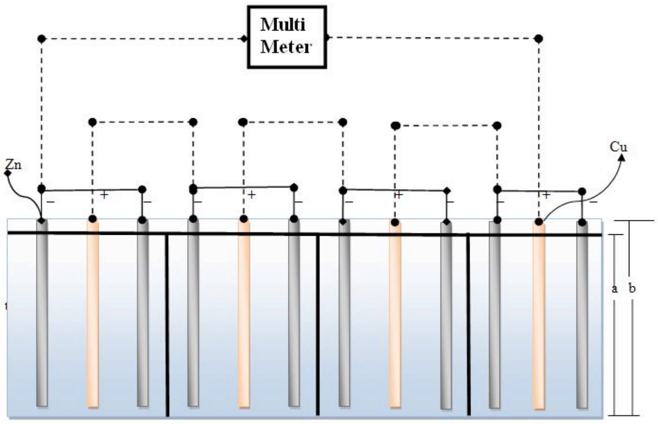

Fig. 4. Arrangement of a bio-electrochemical cell (anode: cathode ratio 2:1) where dotted and plane lines indicate series and parallel connections respectively. Symbols ‘a’ and ‘b’ denote effective height of the electrolyte and cell height respectively.

Table 2. Accuracy of measuring instruments.

Measuring instruments	**Measuring range**	**Accuracy**
pH meter (HI 98130)	0.0 – 14.0 pH	± 0.05 pH
Conductivity meter (HI 8033)	0.0 – 199.9 µS/cm	± 1%
Digital multi-meter (FLUKE-87-V)	0.0 – 10A (ac and dc) 0.0 – 1000V (ac and dc)	± 0.05% dc

3. Results and Discussion

3.1. Bio-electrolyte Investigation

Primarily selected organic-acid-rich bio-electrolytes were tomato juice, tamarind juice and milk whey. Their suitability was studied on the basis of some properties like pH, electric conductivity, economic value and availability.

Table 3. Properties of bio-electrolytes.

Organic source (Fresh)	**Whey**	**Green Tomato** (*Solanum lycoperscium*)	**Red Tomato** (*Solanum lycoperscium*)	**Tamarind** (*Tamarindus indica*)
pH	3.1-3.3	3.6	3.9	3.0
Conductivity (µS/cm)	4.6	3.6	3.2	4.77

The pH of the bio-electrolytes is very close, but conductivity of whey and tarmarind juice are relatively higher compared to that of Tomato juice (Table 3). Therefore, subsequent study was carried on with whey. Milk whey is the by-product of cheese production. Whey is an acidic, yellow-green liquid which is the residue obtained from the coagulation of milk by rennet or by the lowering of its pH [17].

Bio-electrolyte solution can be affected easily by bacterial attack when no preservative is added. After a few days, whey is found contaminated with the pungent smell of the compact layer on the surface. Subsequently, two prominent treatments were taken to preserve the collected whey (i) treatment with antimicrobial reagent (2% Phenol) and (ii) thermal treatment. Fresh whey was compared with treated samples in terms of microbial growth. Comparative studies showed that fresh bio-electrolyte was affected by microorganism very quickly. On the other hand, thermal treatment could save bio-electrolyte from microbial attack for two days, but 2% phenol represents more effectual to preserve bio-electrolyte, it could save more than four days. Additionally, initial pH of the electrolyte plays an important role to generate electricity [18]. Therefore, initial pH and their color/appearance changes were also observed in terms of these two preservation techniques with time. The investigation revealed that prior to the operation, preservation techniques did not have any influence on the initial pH of the whey. After end of the 24 hours of operation with 2% phenol treated electrolyte, the suspended solid (SS) decreased and the total dissolves solid (TDS) increased. The pH of the electrolyte also increased during the operation. Throughout agitation, the temperature of the electrolyte increased continuously because the diaphragm pump was not run with full open discharge. Therefore, into the casing of the diaphragm pump some kinetic energy was converted into the thermal energy. Thus, the temperature of the electrolyte gradually increased from 30 to 45 ºC during operation. It is known that the solubility of a solvent is increased by increasing the temperature. During the experiment, the solubility of the bio-electrolyte was increased when the total dissolve solid also increased from 24.8 to 28.73 g/L (Fig. 5).

Due to the high amount of suspended solid in electrolyte, each compartment behaves as a settling chamber during the experiment. As a result, large number of suspended solids deposited at the bottom of the compartment, but the total suspended solid of electrolyte is reduced from 4.7 to 2.67 g/L (Fig. 5) due to increasing temperature and baffle agitation effect. The pH of the electrolyte increases from 3.1 to 4.6. That means the acidity of the electrolyte was decreased with time. The color of the electrolyte was changed from greenish to pale green (Fig. 2(B)). Hence, it could be concluded that this process has a positive effect on the environment.

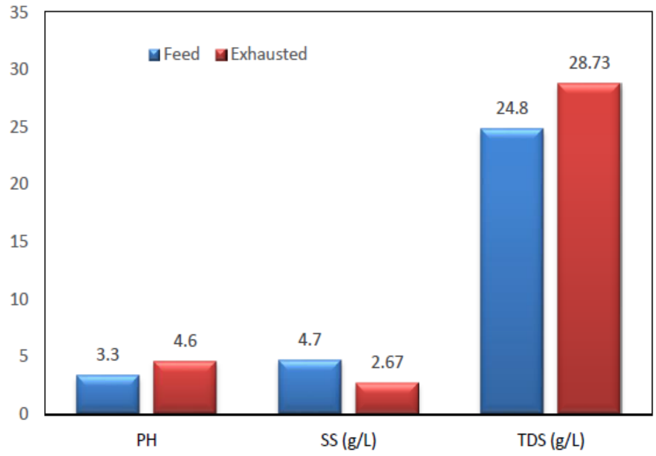

Fig. 5. Comparison study between 2% phenol treated feed electrolyte and exhausted electrolyte.

3.2. *Effect of Surface Area of Anode*

Generation of electricity not only depends on the initial pH of electrolyte, but also depends on the electrode surface area. The larger electrode surface area enhances not only current density [19], but also the pH of the electrolyte. Acids react with anode and produce complex salts (solid corrosion products) forming a layer on the inserted surface of the anode, acting as a barrier to further oxidation [20]. Presence of solid corrosion products resists proton transport through the electrolyte causing internal resistance in the cell [21].The power output can be increased by lowering the internal resistance on the electrodes. The internal resistance is reduced by increasing the anode surface area, and hence rises the voltage and power density [22]. Therefore, cells were designed by increasing anode area for 2:1 ratio of anode to cathode. There are four chambers in each cell-box, and each chamber was arranged in a combination of the two anodes and one cathode system. The inter-links between anode and cathode in separate chambers were the combination of series and parallel connections (Fig. 4). Every electrochemical cell faces internal resistance due to the electrodes and the electrolyte. Larger electrochemical cell of having large electrode contact area with the electrolyte means the less internal resistance it will have [21]. If the area of the electrode is too small, a large internal resistance can be established, possibly because of solid corrosion product. Such resistance can decrease the amount of current generation [21]. The major problem of electrochemical cell is increase of internal resistance within the electrolyte. According to Wiedeburg's theory, the current generation decreases with an increase in internal resistance [23].

Therefore, electrolyte resistance plays an important role in case of electrolyte selection. The lower the internal resistance enhances the better performance of the cell. For this reason, the effect of internal resistance was observed precisely, and a fixed resistor (50 Ω) was connected in parallel and series with the cell while voltage and current were measured, respectively. Fig. 6 illustrates that initially internal resistance is very close for the both 1:1 and 2:1 anode-cathode system. After 24 hours of operations, it has been observed that there is a significant difference between 2:1 and 1:1 anode-cathode system. Hence, it is clear that less surface area and slow reaction rate are responsible to increase the internal resistance in 1:1 anode-cathode system.

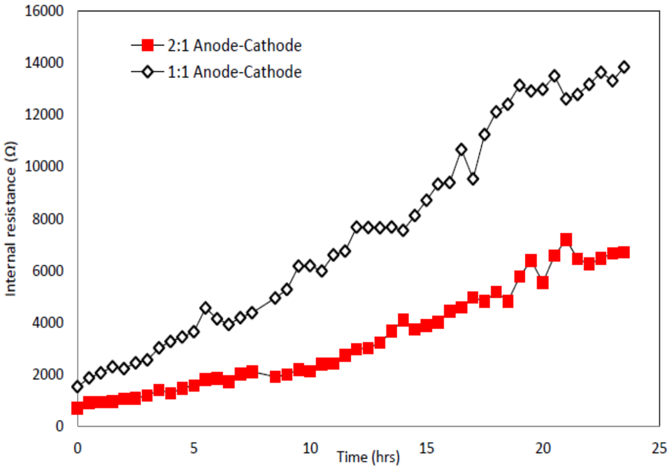

Fig. 6. Influence of anode surface area on internal resistance.

Fig. 7 shows that initially the voltage is remarkably amplified due to increase of anode surface area. After passing few times, voltage gradually decreases for both cases (2:1 and 1:1 anode-cathode systems), but there is a significant difference between two combinations. Comparatively, 2:1 anode-cathode system shows better output than 1:1 anode-cathode system after 24 hours of operations in agitation assisted bio-electrochemical reactor. Moreover, the initial power density was investigated very high (Fig. 8) when the surface area of anode was increased. It might happen due to the reduction of internal resistance with increase of electrode surface area and hence minimize the polarization. The maximum output of power, voltage, current and internal resistance are highlighted (with uncertainty) in Table 4 for milk whey electrolyte with agitation assisted 2:1 anode-cathode system during the 24 hours of operation.

Table 4. Maximum power, current, voltage and internal resistance measurement for whey electrolyte with agitation assisted 2:1 anode-cathode system.

Operating variables	Experimental maximum output	Uncertainty
Power (P)	0.233W	± 0.052 W
Current (I)	0.0134 A	± 0.001A
Voltage (V)	17.35 volts	± 0.2 volts
Internal resistance (r)	695 Ω	± 4 Ω

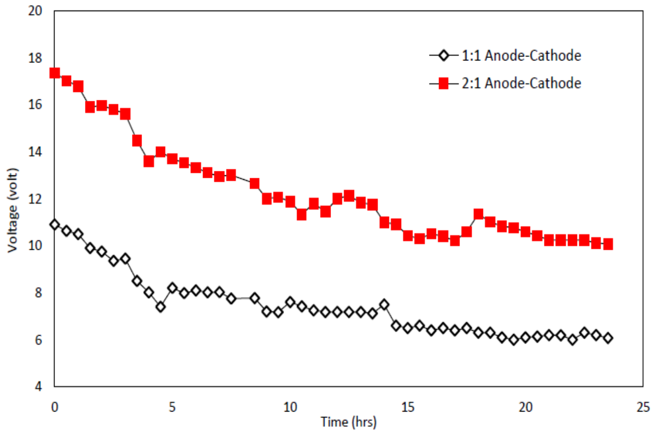

Fig. 7. Influence of anode surface area on voltage.

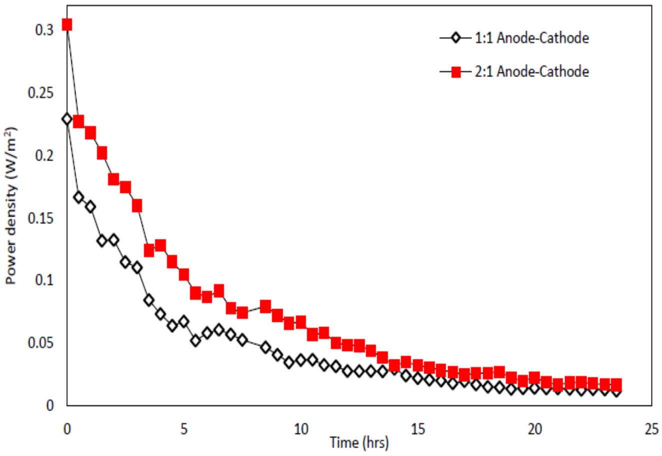

Fig. 8. Effect of anode surface area on power density.

3.2. Comparison between EEs and CEs

The suitability of CEs was compared to that of EEs by using 2% phenol treated whey where the total volume of bio-electrolyte for a single container (Fig. 4) was 1.25 Liter. The Fig. 9 shows the clear difference between the performance of experimental electrodes and commercial electrodes in terms of voltage.

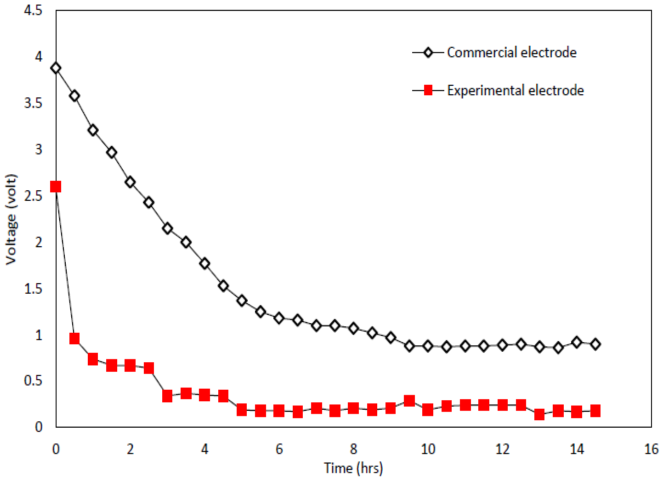

Fig. 9. Trend of voltage change for EEs and CEs.

CEs are much more effective than EEs for the same connection and the same volume of bio-electrolyte. For a single box of containing four unit cells, CEs generate huge current, voltage and power compared with the EEs. The maximum power (Pmax) obtained for experimental electrode was 0.12376 W and maximum voltage (Vmax) was 2.6 V, whereas for CE the values were Pmax = 0.30264 W and Vmax= 3.88V, respectively.

The internal resistance rapidly increased and reached at peak within 15 hours of operation for EEs. On the other hand, internal resistance was increased slowly for CEs (Fig. 10) and maximum value of internal resistance was obtained only 30 Ω. Therefore, commercial electrodes are much more economical and efficient to generate electricity from the bio-electrochemical cell.

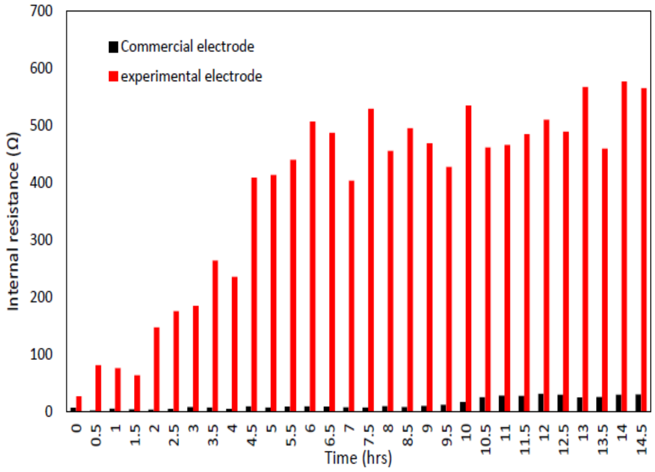

Fig. 10. Variation of internal resistance on CEs and EEs.

4. Conclusion

Among various bio-electrolytes, whey was chosen considering the availability and environmental aspects. To generate efficient electricity, the most significant factors are agitation effect, pH, conductivity and surface area of the electrodes. We obtained maximum 17.35 volt from 6.5 litres of whey by using baffle agitated bio-electrochemical reactor of 2:1 anode-cathode system during 24 hours of operation. The average electricity generation rate was approximately 3.70 volts per hour from a litre of electrolyte. For rural and remote area, such type of electricity generation can be a prominent source of eliminating power crisis. The electricity will be generated continuously until the anode plates get totally corroded. Mostly, the maximum voltage was found at the beginning of the electrochemical reaction because anodes were initially more active to donate electrons. After that, consecutively, anodes are corroded and lost its ability to donate electrons. Ultimately, the electricity production will be reduced slightly at the end of operating hours. Electrification with this technology will lead low investment and less power losses associated with transition and distribution network. The development and modification of electrode can increase the potentiality of bio-electricity production and need more study to make the process simple and practicable. This approach is also able to accelerate the recovery of the power crisis in rural and remote areas.

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