Brackish Water Desalination Coupled With Wastewater Treatment and Electricity Generation

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ABSTRACT

A new bio-electrochemical system was proposed for simultaneous removal of organic matters and salinity from actual domestic wastewater and synthetically prepared saline water, respectively. The performance of a three-chambered microbial osmotic fuel cell (MOFC) provided with forward osmosis (FO) membrane and cation exchange membrane (CEM) was evaluated with respect to the chemical oxygen demand (COD) removal from wastewater, electricity generation, and desalination of saline water. The MOFC wasinoculated with activated sludge and fueled with actual domestic wastewater. Results revealed that maximum removal efficiency of COD from wastewater, TDS removal efficiency from saline water, power density, and current density were 96%, 90%, 30.02 mW/m^2, and 107.20 mA/m^2, respectively.

Key words: microbialfuel cell, desalination, osmosis, electricity generation, wastewater.

تحلية المياه المالحة مقترنة بمعالجة مياه المخلفات وتوليد الطاقة الكهربائية

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الخلاصة

تم اقتراح تنفيذ منظومة احيائية كهروكيمياوية جديدة لأزالة المواد العضوية والملوحة من مياه الصرف الصحي الحقيقية والمياه المالحة المحضرة ، على التوالي. تم تقييم اداء خلية الوقود الاحيائية التناضحية ثلاثية الحجرات والمجهزة بغشاء تناضحي امامي (FO) وبغشاء أيوني (CEM) يسمح بمرور البروتونات على اساس ازالة المحتوى الكيميائي للاوكسجين (COD) من مياه الصرف، وتوليد الكهرباء وازالة الملوحة من الماء المالح. تم استخدام الحمأة المنشطة كمصدر للبكتيريا واستخدام مياه الصرف الصحي كمصدر وقود حيوي مستمر للخلية. اظهرت النتائج المختبرية لمنظومة الوقود الاحيائية التناضحية العاملة بالماء الملحي المحضر نسبة ازالة متطلب اوكسجين كيمياوي، كفاءة ازالة الاملاح الذائبة، كثافة القدرة، وكثافة التيار. كانت 96%، 90%، 30.02 ملي واط/$م^2$، 107.20 ملي امبير/$م^2$ على الترتيب.

الكلمات الرئيسية:خلية الوقود الاحيائي، ازالة الملوحة، التنافذ، توليد الكهرباء، مياه الصرف ا لصحي.

1. INTRODUCTION

It is well recognized that alternative sources of energy are urgently required. Current reliance on fossil fuels is unsustainable due to pollution and finite supplies. While much research is being conducted into a wide range of energy solutions, it does not appear that any single solution will be able to replace fossil fuels in its entirety. However, different alternatives will be required providing energy for a specific task in specialized ways in various situations, **Franks, and Nevin, 2010**.Microbial fuel cell (MFC) technology is a promising approach for wastewater treatment because of its potential energy-creating benefits, and its diverse functions. The anode of an MFC can treat various wastewaters and wastes, including municipal and industrial wastewaters, petroleum wastes, and solid wastes. The cathode can be used to conduct denitrification, or the removal of heavy metals. MFCs that can accomplish contaminant removal, bioenergy production, and clean water extraction will become more competitive with existing wastewater treatment technologies.Extracting clean water from wastewater has been realized by using technologies such as forward osmosis (FO).

FO is the movement of water across a semi permeable membrane in order to induce flow from an area of high-water potential to an area of low-water potential. The driving force in the FO process is the concentrated solution (draw solution) on the permeate side of the membrane, which should have a high osmotic efficiency, and can be easily and inexpensively separated from the solution, leaving potable water. The advantages of using FO include low hydraulic pressure, high rejection of a wide range of contaminants, and less membrane fouling compared with pressure-driven membrane processes, **Zhang, et al., 2011**. A novel microbial osmotic fuel cell (MOFC) has been developed to simultaneously treat wastewater, extract clean water, and produce bioelectricity. MOFCs integrate both FO and MFCs into one bioreactor by replacing ion exchange membranes with FO membranes. This change helps to realize the extraction of high-quality water from the wastewater during the electricity-generating process, **Zhang, and He, 2012**.The use of MOFCs represents a new approach for desalination, but the operational conditions and reactor designs have varied widely. Wastewater can be a good source for energy to desalinate salt water, but acetate has been used as the fuel for most studies in order to create uniform operating conditions for testing desalination aspects of the system performance, **Kim, and Logan, 2013. Zhang, and He, 2013,** developed a system consisting of two membrane-based bio-electrochemical reactors to treat artificial wastewater and desalinate saline water. The coupled system significantly improved desalination efficiency through both dilution (in the MOFC) and salt removal in the microbial desalination cell (MDC) and achieved more organic removal than an individual MDC. It was found that the COD removal 85% and energy production 0.160 kWh/m^3could be achieved. **Werner, et al., 2013,** developed an air-cathode microbial osmotic fuel cell (MOFC) which has a forward osmosis (FO) membrane situated between the electrodes that enable desalinated water recovery along with power generation. The performance of this new design was compared to conventional microbial fuel cells containing a cation (CEM) or anion exchange membrane (AEM). Internal resistance of the MOFC was reduced with the FO membrane compared to the ion exchange membranes; resulting in a higher maximum power production of 43 W/m^3 compared to 40 W/m^3 and 23 W/m^3obtained with AEM and CEM, respectively. The initial water flux declined by 28% from cycle 1 to cycle 3 of operation but stabilized at 4.1 LMH over the final three batch cycles. It is shown that MOFCs have less change in electrolyte solution pH compared to those with AEM and CEM membranes. **Pardeshi, and Mungray, 2014,** investigated the performance of a laboratory made FO membrane in MOFC treating glucose as substrate and 2M NaCl as draw solution. The FO membrane was able to achieve 18.43 lm^{-2} h^{-1} (LMH) water flux and for fouled FO membrane it

was 15.26 lm^{-2} h^{-1}. The MOFC constantly produced bioelectricity and achieved maximum current density of 139.52 A/m^3 and power density 27.38 W/m^3. The energy production of MOFC was 0.438 kWh/m^3.

The present study aimed to investigate the performance of a continuously operated three-chambered microbial osmotic fuel cell (MOFC) for simultaneous wastewater treatment, saline water desalination, and power generation. The MOFC was fueled with actual domestic wastewater and inoculated with freshly collected activated sludge.

2. MATERIALS AND METHODS

2.1 MOFC System

The proposed MOFC consisted of three chambers: the anode, a mid desalination chamber, and the cathode chamber. The bio-electrochemical reactor was made from Plexiglas sheets, which were assembled with silicon tape. The anode compartment was placed at the left side with dimensions of 15 cm x 15 cm x 20 cm. The mid desalination cell had dimensions of 15 cm x 15 cm x 10 cm and the cathode chamber was placed at the right side with dimensions of 15 cm x 15 cm x 20 cm. The anode chamber had three ports, one for wastewater inlet, the other for treated effluent, and the third for nitrogen flushing. The mid chamber had only two ports one for the brackish water inlet, and the other for discharging the treated brackish water. The cathode chamber had three ports, one for catholyte inlet, the other for catholyte replacement, and the third port for air sparging. The mid chamber had two membranes, FO membrane placed between the mid and the anode chamber and CEM membrane placed between the mid and cathode chamber. This was achieved by sandwiching each membrane between two perforated Plexiglas sheets containing 100 holes, each of 5 mm diameter distributed uniformly.Four identical plain uncoated graphite plates were used as electrodes for both anode and cathode. The dimensions of each electrode were 13 cm x 12 cm x 0.3 cm with a total surface area for each electrode of 653 cm^2 in each chamber. The graphite electrodes were abraded by sand paper to enhance bacterial attachment. These electrodes were connected with copper wires by alligator clamps in order to provide connections to an external electrical circuit, through which the electrons were transferred. Before using the electrodes in the MOFC, they were soaked in deionized water for a period of 24 h.

2.2 Substrate, Inoculums, and Chemicals

Actual domestic wastewater samples were freshly collected from the outlet of the primary clarifier at Al-Rustamia Wastewater Treatment Plant (Baghdad) to continuously operate the MOFC system. The quality of actual domestic wastewater is given in **Table 1**.

The brackish water in this study represents the draw solution used in the mid chamber.This solution was prepared by dissolving 130000 mg NaCl, 10000 mg KCl, and 8000 mg $MgSO_4$ in one liter of distilled water resulted in a total TDS of 148000 mg/L.

The MOFC was inoculated with activated sludge samples collected from the bioreactor of Al-Rustamia Wastewater Treatment Plant. The collected sludge was considered as the source for the active biomass.

To enrich the microorganisms growth in the MOFC, mineral salts medium (MSM) was used. The MSM solution was prepared according to the procedure outlined in **Jang, et al., 2004**. The solution was prepared by dissolving 0.56 g $(NH_4)2SO_4$, 0.20 g $MgSO_4 \cdot 7H_2O$, 15 mg $CaCl_2$, 1 mg $FeCl_3 \cdot 6H_2O$, 20 mg $MnSO_4 \cdot H_2O$, 0.42 g $NaHCO_3$ in one liter distilled water, and then the solution was autoclaved at 121◦C for 20 min and cooled under oxygen-free nitrogen gas before use. The catholyte solution was used as an oxidant at the cathode chamber of the MOFC. The

catholyte was a phosphate buffer solution (PBS) consisted of 20.7492 g/L Na_2HPO_4, 3.1167 g/L NaH_2PO_4, and 32.930 g/L of $K_3Fe(CN)_6$ prepared according to **Wei, et al., 2011**.

2.3 Set Up of MOFC

Before the construction and set up of the MOFC system, all the components of the microbial fuel cell were cleaned very well with proper detergent, significantly and repeatedly rinsed with tap water, and then with distilled water.

The CEM membrane was soaked in a sodium chloride solution for 24 h before use. The FO membrane was soaked in deionized water for 30 min (as per manufacturer's instructions). When testing the FO membrane, extensive care was taken into consideration to ensure that the active layer was oriented toward the feed solution, with support layer oriented toward the draw solution. During the assembly of the MOFC, both the anodic and cathodic compartments were filled with deionized water, gently shaken, and then emptied followed by tight closing of the ports. The anode in particular, was pre-treated and sterilized with boiled distilled water for 1 h, and then washed and re-treated for additional 30 min using refresh boiled distilled water to insure the sterilization process.

2.4 Operation of MOFC

Inoculation of MOFC with active biomass at anaerobic condition was achieved by first; flushing the anode chamber with nitrogen gas for not less than 30 min, and then the biomass was added to the anodic section. The biomass was kept in the anode chamber for 14 days, before fueling the MOFC with the actual wastewater as the substrate which was fed continuously to the anode chamber at a constant rate of 2.72 cm^3/ min providing a hydraulic retention time (HRT) of 28 h. At the same time air was purged into the cathode chamber at a rate of 100 cm^3/ min.

Measurement of dissolved oxygen concentration in cathode chamber indicated saturated concentrations which improves the reduction reaction. While in the anode chamber, the dissolved oxygen concentration was observed to be almost zero indicating the existence of anaerobic conditions in the anode chamber.

The TDS and conductivity of the brackish water were continuously observed and measured at the mid chamber to evaluate the MOFC performance with respect to the desalination of brackish water with time.

Water flux from the anode chamber to the mid chamber was measured by using a digital scale recording the change of water flux within a certain period of time. Water flux was either expressed in mL or calculated as liter per surface area of the FO membrane per hour (LMH).

The performance of wastewater treatment with respect to the chemical oxygen demand (COD) concentration was carried out by daily sampling of both influent and effluent of wastewater in the anode chamber.

2.5 Analytical Techniques and Calculations

2.5.1 Power calculations

The power generated by a MFC is quantified in terms of power output as follows, **Barua, and Deka, 2010**:

$$\boldsymbol{P = V_{cell} .I} (1)$$

The current produced in MFC is calculated by measuring the potential across the load (i.e. the external resistor, R_{ext}) and by using Ohm's Law, **Logan, 2008**:

$$I = \frac{V_{cell}}{R_{ext}} \quad (2)$$

Thus, the power output can be calculated by:

$$P = \frac{V_{cell}^2}{R_{ext}} \quad (3)$$

Where: P = power (W), V_{cell} = cell voltage (Volt), I = current (Amp), R_{ext} = external resistance (Ω).

2.5.2 Power output normalized by surface area

Knowing how much power is generated by a MFC does not sufficiently describe how efficiently that power is generated by the specific system architecture. Thus, it is common to normalize power production by the surface area of the anode, so that the power density produced by the MFC is calculated by using Eq. (4)**, Shukla, et al., 2004**:

$$P_{An} = \frac{V_{cell}^2}{A_{An} \cdot R_{ext}} \quad (4)$$

Where: P_{An}= power density (W/m^2), A_{An} = anode surface area (m^2)

3. RESULTS AND DISCUSSION

3.1 Substrate Removal from Wastewater

The profile of COD removal from actual wastewater is given in **Fig. 1**.The COD removal efficiency was observed for 30 days. The COD loading rate was 0.54 kg COD/m^3 d.Maximum COD removal > 96% was observed after 13 days of continuous operation, and then a steady state condition was achieved after almost 15 days with an average COD removal efficiency of 90%.These findings were comparable to the maximum COD removal up to 90% reported by **Werner, et al., 2013,** for a microbial osmotic fuel cell operating with acetate-based synthetically prepared wastewater and NaCl solution as the draw solution.Biological oxygen demand (BOD) was measured along with to the chemical oxygen demand (COD) measurements. Maximum BOD removal was observed achieving 72% as given in **Fig. 2**.

3.2 Electricity Generation

The system was continuously operated for 30 days; the open circuit potential was 0.424 volt. For the closed circuit, the operation of MOFC consisted of 4 phases **Fig. 3** and **Fig. 4**, a rapid increase in potential difference and current generation up to 0.28 volt and 7.0 mA was observed at the 5th day. This rapid increase is due to the high proton transfer resulting from high water flux between the two sides of the FO membrane. After 5 days, the potential and current maintained stable with a slight decrease until a rapid decrease appeared after 17 days of operation. This observation was most likely due to the water flux reduction resulting from the FO fouling which restricted the protons transfer through the FO membrane, and then a stable condition was observed after 21 days operation due to the fact that the FO membrane was significantly fouled. The maximum obtained power density and current density were 30.02 mW/ m^2 and 107.2 mA/ m^2, respectively as given in **Fig. 5**.

3.3 Brackish Water Desalination

Results revealed that the initial TDS concentration (148000 mg/L) in the draw solution was reduced by more than 91 ± 1% (**Fig. 6)**.These results are more favorable than the maximum TDS removal of 57.8% previously reported by **Zhang, and He, 2012** for an osmotic microbial desalination cell (ODMC).

4. CONCLUSIONS

This study demonstrated the validity of using a hybrid design of microbial osmotic fuel cell (MOFC) for simultaneous biotreatment of wastewater, desalination of brackish water, and generating bioelectricity as well. Significant relationship between COD removal from wastewater and power generation was obtained in the MOFC fed with real domestic wastewater indicating the validity of this bio-electrochemical system for the treatment of actual effluents.Results demonstrated that the highest removal efficiency of COD from wastewater in MOFC was up to 96% after 14 days of continuous operation. Experimental results indicated that FO membrane fouling has a superior effect on the MOFC performance with respect to electricity generation. A drop in the voltage, mainly due to FO membrane fouling was observed in MOFC after 17 days of continuous operation. Desalination of brackish water reached 91% which is more than the reported results in ODMC.

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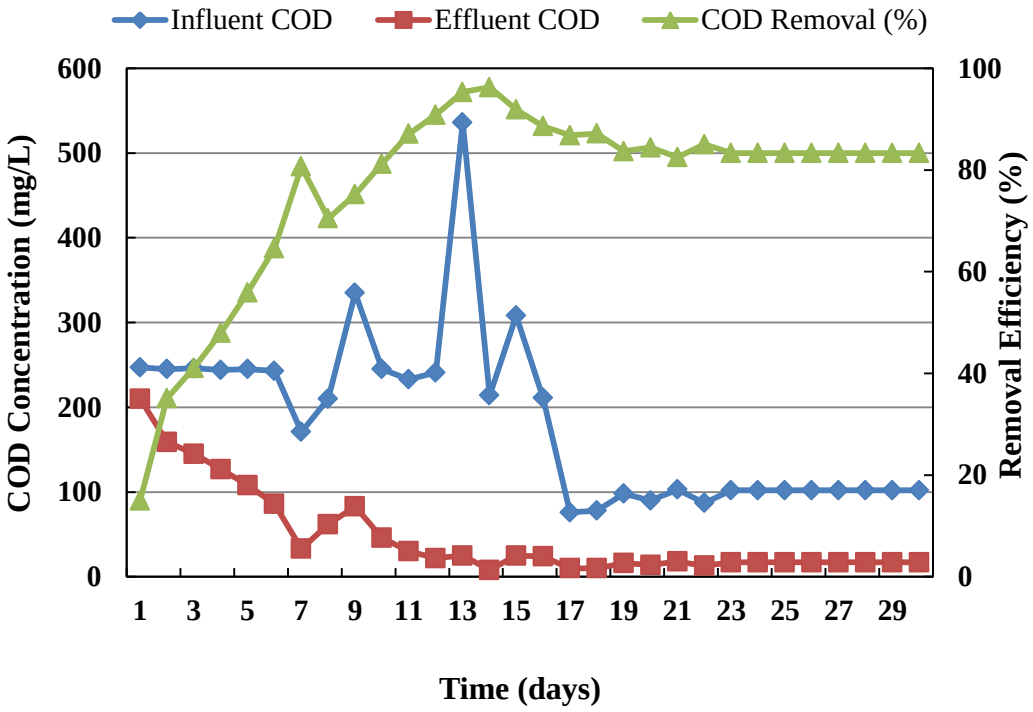

Figure 1. Profile of COD removal

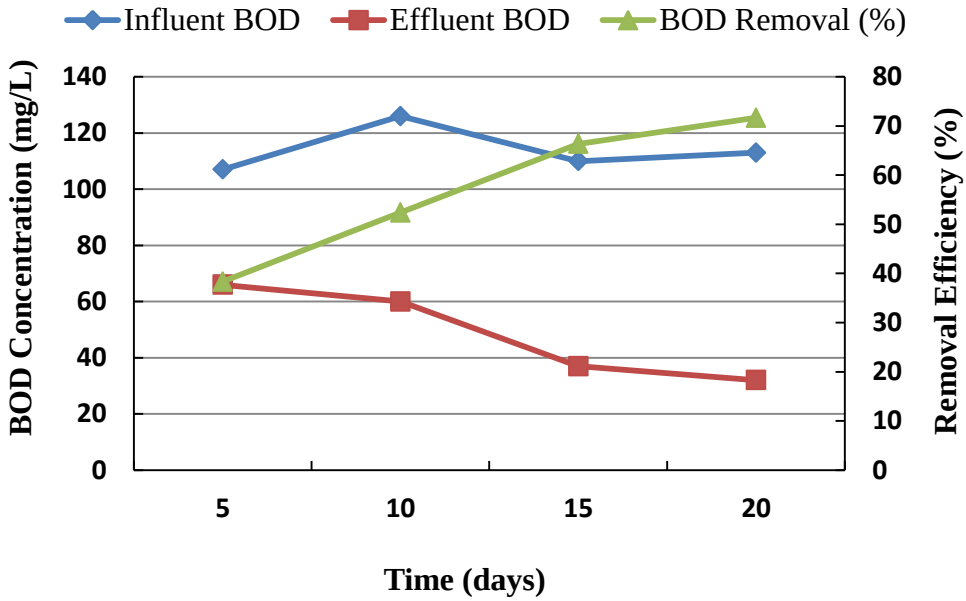

Figure 2. Profile of BOD removal efficiency

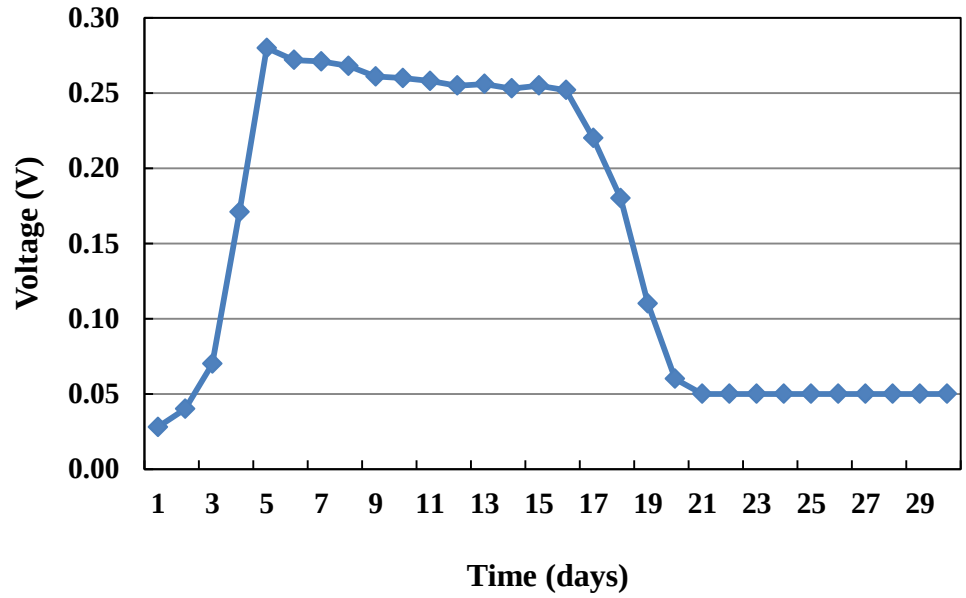

Figure 3. Variation of voltage with time

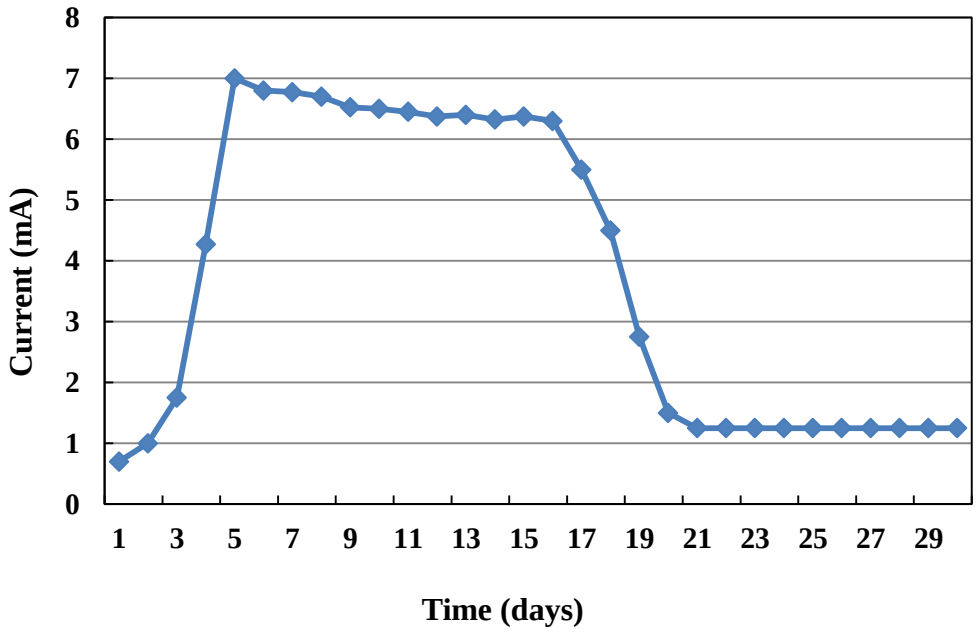

Figure 4. Variation of current with time

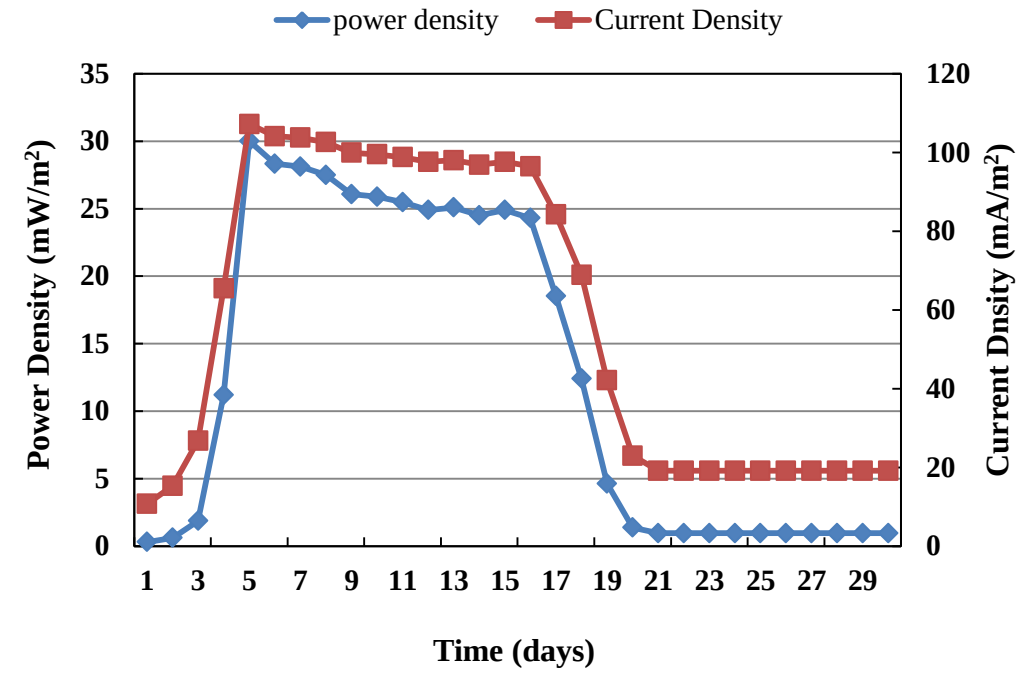

Figure 5. Variation of power and current densities with time

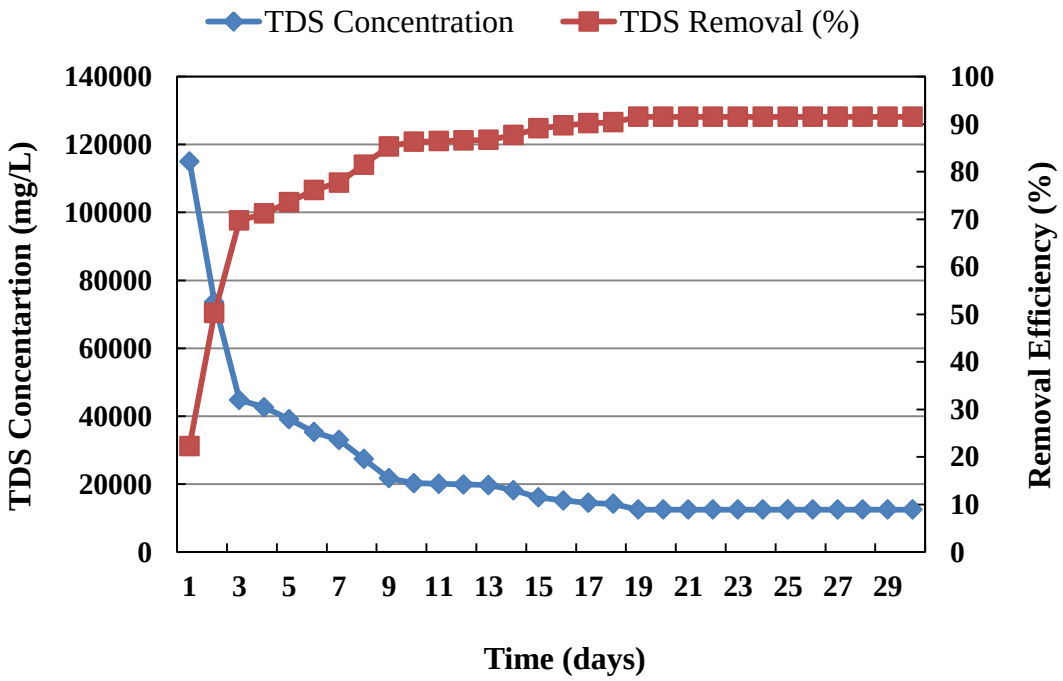

Figure 6. Profile of TDS removal

Table 1. Quality of the actual domestic wastewater

Constituent	Unit	Average concentration
BOD	mg/L	129
COD	mg/L	246
TSS	mg/L	105
TDS	mg/L	1750
PO_4^{-3}	mg/L	23.8
NO_3^-	mg/L	30
Cl^-	mg/L	625
SO_4^{-2}	mg/L	850
pH	---	7.3-7.7
Conductivity	µS/cm	2.57