BIOELECTROCHEMICAL TREATMENT MECHANISMS OF PETROLUME REFINERY WASTEWATER IN INTEGRATED SYSTEM OF MICROBIAL FUEL CELL-CONSTRUCTED WETLAND

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ABSTRACT

Three identically designed systems named designate as MFC-CW, CW1,and CW2 were constructed and setup in this study for simultaneous biotreatment of real petroleum refinery wastewater (PRW) and bioelectricity generation. The three systems were planted with emergent wetland plant of C*anna indica*. These systems were operated simultaneously in a single batch mode to identify the dominant mechanism for organics removal from PRW. The operation period for each cycle was 8 days. Results demonstrated that maximum removal efficiency of the organic content represented as chemical oxygen demand (COD) were 96.5%, 89.3%, and 91% observed in MFC-CW, CW1, and CW2, respectively, whereby, the highest power generated in MFC-CW only was 12.36 mW/m^2. The potential convergence of the results in the three systems indicated that the dominant mechanism of organic content removal from PRW was via bioelectrochemical reactions by the anodic biofilm in the MFC.

Keywords: biotreatment, organic content removal, wetland plant, power production, wastewater.

المعالجة الحيوية– الكهروكيميا وية للمياه العادمة من مصافي النفط في نظام متكامل للأراضي الرطبة المشيدة مع خلايا الوقود الحيوي

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المستخلص

تم في هذه الدراسة تصميم ونصب ثلاثة منظومات متماثلة التصميم ونوع النبات المستخدم. الاولى تحاكي النظام المتكامل للأراضي الرطبة المشيدة – وخلية الوقود الحيوي ،بينما تحاكي المنظومتان الثانية والثالثة الارضي الرطبة فقط بهدف تحديد الالية المسيطرة في معالجة نماذج حقيقية من المياه العادمة الناتجة من مصافي النفط وانتاج الطاقة الكهربائية في آن واحد. تم زرع المنظومات الثلاثة بنبات القنب الهندي وتشغيل المنظومات الثلاث بنفس الوقت على اساس النظام الدفقي وبدورة واحدة وبفترة تشغيل ثمانية ايام. اوضحت نتائج الدراسة ان اعلى كفاءة ازالة للمحتوى العضوي والمتمثل بطلب الأوكسجين الكيميائي كانت 96.5%, 89.3%, و91% للأنظمة MFC-CW, CW1 , و CW2 على التوالي. ان اعظم كثافة طاقة ناتجة كانت 12.36 ملي واط/ م^2 في منظومة MFC-CW , في حين ان المنظومتين CW1, و CW2 لا ينتج عنهما كهرباء. اثبتت هذه الدراسة أن الالية المسيطرة في ازالة المحتوى العضوي في المياه العادمة هي التفاعلات الحيوية– الكهروكيميائية التي تحدث داخل الكتلة الحيوية التي تنمو على قطب الأنود داخل خلية الوقود الحيوي

الكلمات الدالة: المعالجة الحيوية، ازالة المحتوى العضوي، الاراضي الرطبة ، توليد الطاقة الكهربائية، المياه العادمة

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INTRUDUCTION

Nowadays, intensive industrialization together with rapid population growth and economic improvements have raised a growing demand on water sources, and thus wastewater is now being considered as one of the important resources of water, energy, and plant fertilizing nutrients (14, 16) . Refinery operations are quite complex and require large volumes of water, and the composition of refinery wastewaters can vary substantially among different sites (3). However, conventional wastewater treatment plants currently consumes a significant amount of electricity (16). Accordingly, in order to offset the costs of wastewater treatment and save energy, alternative methods are being developed to capture energy or produce useful chemicals from wastewaters (15). Microbial fuel cells (MFCs) can exploit a variety of soluble or dissolved complex organic waste/wastewater as substrate to fulfill renewable electricity generation along with simultaneous waste remediation (8, 23). A complex substrate composition helps in building a diverse and electrochemically active microbial community while a simple substrate is easier to degrade and improves the electricity generation of the system (5). On the other hand, Wastewater treatment utilizing constructed wetlands (CWs) are engineered systems that mimic natural wetlands while adding a series of biological, chemical, and physical purification mechanisms in order to treat wastewater (27, 28, 31). CWs have the advantages of low cost and easy operation, have been thoroughly studied and widely used (13). The integration of CWs with a microbial fuel cell (MFC) technologies shows promise as a new type of wastewater treatment, which is considered to be an economical and effective way of harvesting bioenergy (32). CWs and MFCs can be combined because CWs can provide the redox conditions, anaerobic anodes and aerobic cathodes, required by the microbial fuel cells (7). The chemical transformations occurring at the anode is $CH_2O+nCO_2 \rightarrow nCO_2+4ne^-+4nH^+$. From anode to cathode, electrons pass through the external circuit while protons move inside the system. Then occurring at the cathode is $4ne^-+n/\ 2O_2+4nH^+ \rightarrow n2H_2O$, completed the whole electrochemical cycle (21, 22). In such systems, a combination of plant, bacteria, and substrate is used to treat wastewater and the combination harvests chemical energy in organic matter by electrogenic bacteria in order to generate electricity. This unique operational characteristic of a CW-MFC may make an ideal approach to treating wastewater by removing organic pollutants, as well as generating electricity in the same systems, especially when installations, operation, and maintenance costs are limiting factors for applying other treatment technologies such as conventional methods. Therefore, nowadays, the applications of wastewater treatment and bioelectric production by The first research associated with using CW-MFC for wastewater and bioelectricity production was investigated by Yadav et al. (34) who combined CW systems with MFC to treat dye-laden wastewater. More recently, other MFC devices have been used in other CWs types including those that change levels of organic loads and spacing of electrodes in CW-MFC systems (9,13, 29). *Canna indica* is commonly used for wetland establishment in China and other countries (6, 19) as it has rapid growth rate, large biomass and beautiful flowers with great capability of nutrient removal (11). Previous studies indicated that the presence of the macrophyte increases microbial diversity and provides large surface areas for the development of biofilm (4). Most relevant studies have focused on improving anodic and cathodic efficiency or reducing the internal resistance of the MFC-CW to generate more energy or improve nutrient removal efficiency from wastewater (9, 10). Electrochemically active bacteria (EAB) are generally considered to be the major factor leading to fluctuation of bioelectricity and changes of the microbial community structure in CW-MFCs (32). The response to additions of substrate when immobilized bacteria were used was faster than that achieved with freely suspended organisms. This is attributed to the advantageous mass-transfer kinetics resulting from the proximity of the immobilized bacteria and the electrode surface (1).

This study was aimed to investigate the followings:

1- The potential of simultaneous biotreatment of real petroleum refinery wastewater (PRW) biotreatment and bioelectricity generation in an integrated system of MFC-CW.

2- Identify and characterize the dominant mechanisms for COD removal from PRW in the MFC-CW systems, whether it is biodegradation by the anodic biofilm or phytoremediation process.

MATERIALS AND METHODS

Substrate

Fresh petroleum refinery wastewater (PRW) was used to fuel the microbial fuel cell in this study. The samples were freshly and continuously collected from Al-Dora refinery in Baghdad. Table 1 presents the quality of this industrial wastewater in terms of Chemical oxygen demand (COD), pH, and Total suspended solid (TSS) Total petroleum hydrocarbon (TPH), phosphate ions (PO^{-4}), chloride ions (Cl^-), sulfate ions (SO_4^{-2}), copper (Cu), lead (Pb), zinc (Zn), and cadmium (Cd). The PRW is characterized by its high organic content as COD concentration is up to 1200 mg/l, and total petroleum hydrocarbons of 480 mg/l. The characteristics of PRW were determined according to the procedure outlined in the *standard methods* (2).

Biocatalyst

Activated sludge freshly collected from the existing wastewater treatment plant in Al-Dora refinery was used to inoculate the anodic section of the MFC embedded with the CW. Analysis of the collected sludge samples indicated that *Bacilli* species were the dominant type of bacterial cells in the sludge samples. The initial volatile suspended solids (VSS) concentration was 626.6 mg/g which represents the initial concentration of biomass in the sludge.

MFC-CW systems

In this study, three identically designed systems were constructed and set up out door. These systems were named as MFC-CW, CW1, and CW2, and all of them were made of Perspex column of 0.5 cm thickness, 19.5 cm inner diameter and 40 cm height.

Table 1. Characteristics of the real petroleum refinery wastewater (PRW)

Constituent	Unit	Average concentration	Allowable* concentration
pH	-	7.75	6-9.5
COD	mg/l	1200	100
TSS	mg/l	75	30
TPH	mg/l	480	10
CL^-	mg/l	68	200
SO_4^{-2}	mg/l	55	200
PO_4^{-2}	mg/l	7.5	3.0
NO_3^-	mg/l	30	50
Cu	mg/l	Nil	0.2
Pb	mg/l	Nil	0.1
Zn	mg/l	Nil	0. 5
Cd	mg/l	Nil	0.01

*** According to the Iraqi regulation No. 25 in 1976 for rivers and public water reservation.**

The MFC-CW system was filled with gravel as a supporting layer to the height of 37cm as shown in Figure 1. The upper ends of the MFC-CW systems were maintained open to atmosphere. Two identical plain graphite electrodes of 1cm thickness (effective surface area of 526.7cm^2) were used in it. While the other two constructed wetland (CW) systems were designed and constructed of similar dimensions and material as for the CW-MFCs system, but without MFCs. One CW was a conventional type of constructed wetland (CW1) and the other was also a conventional type but with supplemented active microbial cells (CW2). They were fed with the same PRW and operated in a batch wise. according to the suggestion reported by Narayan et al. (18), in order to ensure MFC function efficiently, it is important that the anode compartment maintains in anaerobic condition. Therefore, anode was positioned at the bottom of the reactor fulfilling the suitability of anodic reaction in MFC. While cathode compartment at rhizopheric zone, oxygen must be easily obtained as it will combine with protons from anode and electron from external circuit to complete the circuit. So, the anode electrode was positioned at distance of 10 cm from the bottom in an anaerobic condition. While, the cathode was installed at the plant root zone at 30 cm from the base of the MFC-CW system. Both electrodes were layered between gravels. Each electrode had a projected surface area of 0.0526 m^2. The electrodes were placed horizontally in the system to maintain. the anode zone relatively anaerobic and the cathode zone more aerobic. The total volume of the MFC-CW was 12.56 L (0.01256 m^3) with the total void volume of the system (net liquid volume of 5 L (gravel porosity = 0.43%). A sampling port was located directly above the anodes in each one of all three systems. In this study, MFC-CW, CW1, and CW2 were planted with *Canna indica* plant at a density of 2 plants/ reactor without pre-acclimation, which is a type of emergent wetland plants. In MFC-CW, *Canna indica* was placed on the upper surface of the cathode. The anode and cathode in the MFC were connected to each other using copper wires to an external resistance 100Ω. Before operating the three MFC-CW, CW1, and CW2 systems, each of anodic electrode of MFC-CW and the gravel of lower part of CW2 were inoculated with the biomass in an anaerobic environment with 100 g of biomass, and then continuously monitored for 4 weeks with periodic feeding with the PRW in order to acclimate the biomass for this toxic type of wastewater.

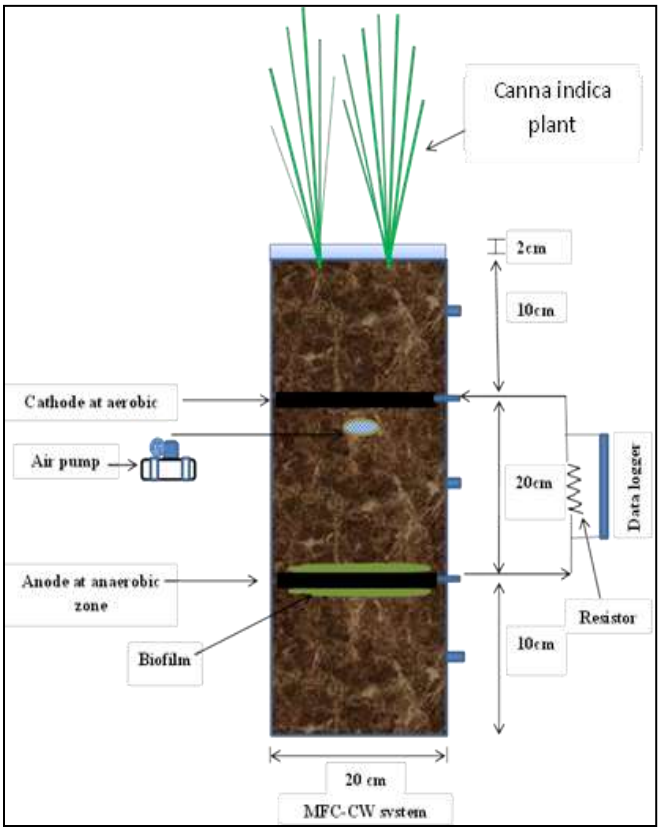

Figure 1. Schematic demonstration of the MFC-CW.

Experimental procedure

After inoculation, the three systems; MFC-CW, CW1, and CW2 were operated in a batch mode at a period of 8 days. The PRW was added to each system from the top and was allowed to firmly trickle through the system. During the operation period, samples of influent and effluent were daily collected for analysis to observe the profile of COD reduction in the MFC-CW systems. Samples of effluent were withdrawn from the sampling port (S2) which was located 15 cm from the base of bioreactor before reaching the plant roots. Also, additional samples of the treated effluent were collected from the sampling port (S3) which was located 28cm from the base of bioreactor after passing through the plants roots.

The contribution of abiotic processes for organic removal

Also, to investigate the contribution of abiotic processes (adsorption) for organics removal, a preliminary side set of batch experiments was conducted to find the potential of gravel, crushed ceramic, and crushed glass for the adsorption of organic content in PRWW of 650 mg/L concentration. This performed in a laboratory using the ratio of (1/3:2/3) as (Gravel:PRWW) in 250 ml conical flask and shacked for a period of 6 h.

Analytical methods

Samples were collected and analyzed on a daily basis for dissolved oxygen (DO), chemical oxygen demand (COD), total dissolved solids (TDS), electrical conductivity (EC) concentrations, and pH values as well. COD analysis was carried out using COD analyzer (Model: RD 125, Lovibond, Germany). DO concentrations were measured using dissolved oxygen meter (Model: DO-5510HA, Taiwan). pH, TDS, and EC value were measured using multi parameters analyzer (Model: Portable Milwaukee, MW 803, Romania). A volatile suspended solid (VSS) measurements were determined according to EPA-1684 Method. All measurements were performed in duplicate.

The COD removal efficiency can be calculated by using the formula below:

$$COD_E = \frac{C_{Inf} - C_{eff}}{C_{Inf}} \times 100\% \quad \ldots\ldots (1)$$

Where; C_{inf} is the COD concentration of the influent, and C_{eff} is the COD concentration of the effluent (mg/l).

Bioaccumulation Factor (BAF) for petroleum hydrocarbon in plant tissues

The concentration of TPH represents the sum of all the Petroleum hydrocarbon (PHC) components in crude oil that were taken up by the plant. Samples of Canna indica plants were harvested from all of them, at the end period of the experimental study to assess TPH uptake by the wetland plant, and separated into above-ground and below-ground biomass. A slightly washed with tap water ,TPH was extracted from plant tissue in an ultrasonic cleaner (Kwunwah International Ltd., China). using dichloromethane, and TPH was calculated gravimetrically while saturated hydrocarbons was analyzed by gas chromatography-mass spectrometry (GC-MS). **(**Model: Agilent Technologies 5977E MSD, USA).

Electrochemical measurements

The cell voltage were monitored in order to determine the power generation and the performance of MFC-CWs. The potentials between the edges of the fixed external resistance (100 Ω) were measured data logger as well as a portable handheld digital multimeter (model: MT-1233C, Proskit, Taiwan) for double checking. Once the voltage outputs of each reactor were stabilized, the electrochemical performance of the systems were analyzed in term of polarization and power density.

The electrical current (I) measured in amperes (A) was calculated by using Ohm's law:

$$I = \frac{V}{R} \quad \text{….. (2)}$$

Where; V is cell voltage (V), R is the external resistance (Ω).

Power was calculated using the following formula:

$$P = I \times V \quad \text{….. (3)}$$

Where;

V is the potential difference between two points which include a resistance R. I is the current flowing through the resistance.

Current density (ID, mA/m^2) and Power density (PD, mw/m^2) were normalized to anode surface area and determined by the Eqs. (4) and (5), respectively.

$$ID = V/(R \times A) \quad \text{….. (4)}$$

$$PD = ID \times V \quad \text{…… (5)}$$

Polarization and power density curves were obtained by varying the external resistance from 100000Ω to 3Ω every 10 min to ensure that the measured values were steady and repeatable. The potential of electrodes was measured using the anode or the cathode as the working electrode against a (SCE) saturated calomel Ag/AgCl reference electrode (Type: Ag-AgCl Beckman Laboratory, USA). and the values were recorded with the digital multimeter.

$$\eta_{Coulombic} = \frac{M\int_0^t I dt_{exp}}{FnV\Delta COD} \times 100 \times 1000 \quad \text{… (6)}$$

Where;

$\eta_{Coulombic}$ = Coulombic efficiency, %

I = Current generated in the MFC system, Ma

t_{exp} = Interval of recording, seconds

t =Total period of the experiment, seconds

F =Faraday's constant, 96485 coulomb/mole

ΔCOD = Difference between the inlet and outlet chemical oxygen demand concentration, (mg/l)

n =Number of electrons exchanged per mole of substrate (eight mole of electrons were produced as acetate oxidation in anaerobic anode chamber).

V =Effective volume of the effluent involved in the work (mL)

M=Molecular weight of the substrate (g/mole).

RESULTS AND DISCUSSION

The dominant mechanism for organics removal from PRWW

Table 2 summarizes the overall performance of the three experimental systems (MFC-CW, CW1, and CW2) in terms of COD removal, power generation, and plant growth. As given in Table. 2, the general performance of the MFC-CW7 system for the treatment of PRW was very significant compared to the CW1 and CW2. The organics removal efficiency in the MFC-CW represented by COD was clearly higher than that in CW1 and CW2 as given in Figure 2. These observations may be attributed to the abundance of electrogenic active bacteria located in MFC-CW system. Similar findings and observations were reported by Xu et al. (33), who investigated pollutant removal and microorganism evolution in CW and CW-MFC. They found that the average removal rates of COD, in CW-MFC were 82.32 ± 12.85%, which was higher than that in CW, which was 75.71 ± 11.24, respectively. As well as Similar to the results obtained by Narayan et al., (18)**,** who investigated the effects of hydraulic residence time (HRT), COD concentration on the electricity production of CW-MFC and the degradation characteristics of pulp and paper effluent with the initial value of COD was 1958.3 mg/L. The highest electricity production was obtained when HRT was 5 day. They obtained a total of 89.09% of COD reduction occurred in their system, and attributed this a drastic reduction of COD to microbes in anodic chamber, where microbes oxidized organic substrate as carbon sources to support microbial activity (17, 30).

Table 2. Performance summery of MFC-CW, CW1, and CW2 systems

Item	MFC-CW	CW1	CW2
Description	Microbial fuel cell coupled with constructed wetland	Conventiona l constructed wetland	Constructed wetland with supplemented bacterial cells
Organics removal	Significant COD removal (96.5%)	Observable COD removal (89.3%)	Observable COD removal (91%)
Electricity generation	Electricity generation (12.36 mW/m^2)	No electricity generation	No electricity generation
Plant growth	Healthy growth with new shoots	No growth, almost didn't survive	Slight growth

However, power generation and healthy plant growth observed just in MFC-CW7 makes this new hybrid system a superior option compared to conventional CW systems. Figure 3 illustrates the maximum power density generation of 12.36 mW/m^2 which was obtained the MFC-CW7 system, whereby, CW1 and CW2 didn't produce any power as mentioned in Table 2.

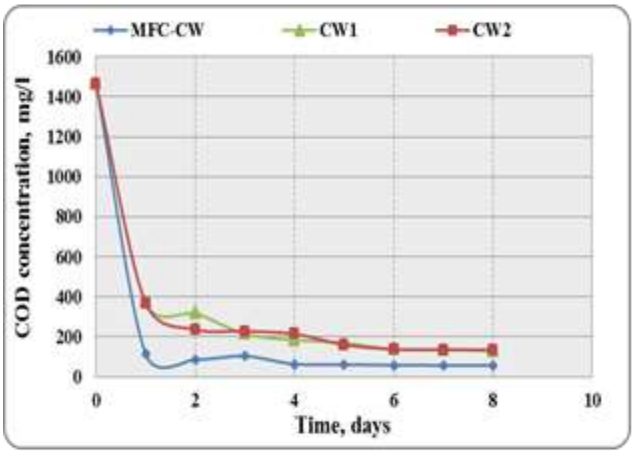

Figure 2. Profiles of COD removal in MFC-CW, CW1, and CW2

On the other hand, in MFC-CW, healthy growth with new shoots was observed, while no growth and unhealthy slight growth were observed in CW1 and CW2, respectively. Generally speaking, the results indicated that bioelectrochemical processes are the dominant mechanisms for organic removal in the MFC-CW systems.

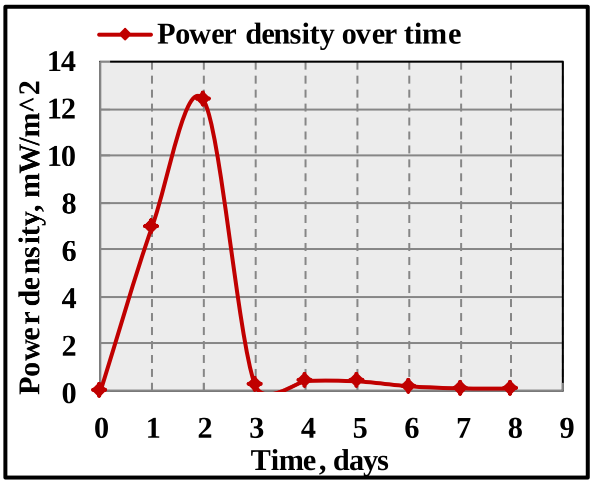

Figure 3. Profile of power density generation overtime in MFC-CW

No detectable concentrations of TPH and saturated hydrocarbons were found in material of the canna indica plant tissues. This may be due to the rapid biodegradation and transformation of hydrocarbons into daughter products., resulting zero value of Bioaccumulation Factor (BAF) for petroleum hydrocarbon in canna indica tissues.

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