# Activated carbon clogging analysis in an integration of constructed wetland with microbial fuel cell

Qiao Yang\*, Chao Gao, Zhen-Xing Wu, Sheng-Na Liang, and Min-Hui Liu

School of Food and Environment, Dalian University of Technology, Panjin 124221, China

**Abstract.** Constructed wetland (CW) is a low cost and easy operation process for wastewater treatment, while filler clogging is one of the disadvantages for this technology. Using activated carbon as the filler, a regular CW and an integration of constructed wetland with microbial fuel cell (CW-MFC) were constructed. After continuous operation of four months, specific surface area and pore size distribution of the activated carbon were analyzed. The specific surface area of the fresh activated carbon was 133.8 m<sup>2</sup>/g, while the filler in the CW and CW-MFC systems had specific surface area of 38.1 m<sup>2</sup>/g and 58.2 m<sup>2</sup>/g. The surface decrease of the CW-MFC filler was 21% lower than that of CW filler. Comparing with the regular CW, the filler in the CW-MFC was more clogging resistant. The alleviation of the filler clogging in CW-MFC may be caused by the micro-electric field as the function of MFC. CW-MFC is a promising microbial electrochemical technology for wastewater treatment and filler clogging resistant, there are some detailed issues deserve to be further researched.

# **1** Introduction

Constructed wetland (CW) has been proven as a promising technology to treat wastewater pollution, and it has been successfully applied to secondary processing treatments of domestic sewage, leachate, rainfall runoff, and industrial effluent [1, 2]. The regular CW is constructed by artificially constructing a pool or a grooved structure, filling in a certain depth of the filler layer, planting aquatic plants, and purifying the sewage by using the triple synergy of the physical, chemical and biological aspects of the substrate, plants and microorganisms. According to the existing data, CW system can not only treat domestic sewage mainly composed of oxygen-consuming organic pollution but also nitrogen, phosphorus and other nutrients. And it has the advantages of low cost and easy operation [3]. However, CW has also exposed some problems that cannot be ignored in the development and application process. Many constructed wetlands have experienced clogging of fillers after a period of operation, which directly leads to a decrease in treatment effect.

Bioelectrochemical methods have been one of the hotspots in the research of pollutant resources and energy in recent years. Microbial fuel cell (MFC) is further categorized from Bioelectrochemical systems (BESs). By constructing MFC, the electrogenic microorganisms in the anode region decompose the organic matter in the water under anaerobic conditions, transfer the generated electrons to the anode, and cooperate with the cathode in which the reduction reaction takes place to obtain a continuous current in the external circuit. The direct conversion of chemical energy in the sewage to electrical energy ultimately achieves the dual effects of electricity generation and decontamination [4]. Besides, BESs can be operated without inputting a large amount of energy, and produce micro electric energy, which have potential application in biosensor for BOD or toxicity detection [5].

The integration of constructed wetland with microbial fuel cell (CW-MFC) technology combines the advantages of the two systems. It promises as a new type of wastewater treatment, which is considered to be an economical and effective way of harvesting bioenergy [6]. In previous study, CW-MFC systems were developed for treatment of sanitary sewage and production of bioelectricity. The average COD removal efficiencies of CW-MFC was about 80%, and the total nitrogen (TN) removal efficiencies were over 65% [7]. When applied to the treatment of azo dye wastewater, the experiment proved that the decolorization rate reached 76%, 81%, 69% and 93% respectively by the degradation of the influent concentration of 2000, 1500, 1000, 500 mg/L wastewater for 96 hours. In terms of electricity production performance, when the influent concentration is 1000 mg/L, the maximum power density is  $15.73 \text{ mW/m}^2$ , and the maximum current density is 69.75 mA/m<sup>2</sup> [8]. A satisfactory effect on oil removal of over 95.7% and the COD removal rate of over 73% was obtained when treat with the oil wastewater [9].

In summary, all above previous CW-MFC studies have good performances on pollution removal efficiencies and power or current generation. However, the problem of the filler clogging in CW has not been studied. In this study, we would focus on this issue and may propose a solution to this problem.

<sup>&</sup>lt;sup>\*</sup> Corresponding author: <u>yangqiao@dlut.edu.cn</u>

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# 2 Experiments and Methods

## 2.1 Construction of the reactors

In this study, regular activated carbon (particle size of 4-6 mm, originate from coconut shell) was used as filler of the CW reactor and the CW-MFC reactor (with a 1000 ohm load in external circuit). The reactors used in this study were settled in a polyacrylic plastic column (250 mm x 110 mm diameter) as shown in Figure 1. Activated carbon were used both as the filler of the CW and part of the cathode of MFC. The top cathode layer comprised carbon felt, activated carbon particles and a graphite plate, which could assist the electrons collection of cathode. The anodes were heat treated carbon brushes and gravel and glass wool were set up to keep the electrodes apart.



Figure 1. Schematic of reactor (1) Inlet pipe. (2) Glass wool. (3)
Gravel. (4) Carbon brush. (5) Gravel. (6) Glass wool. (7)
Activated carbon. (8) Graphite plate. (9) Carbon felt. (10)
Outlet pipe. (11) Resistor.

## 2.2 Reactor Operation

The mixture of domestic sewage and activated sludge was pumped into reactors from the water inlet to make sure the mixed microorganism load on the carbon brush of the anode layer. When the voltage of our reactor came to a stable value, it was confirmed that the biofilm had been formed. The oil-contaminated wastewater was continuously injected through the bottom inlet and finally discharged from the upper outlet of the reactors through a peristaltic pump. They were operated synchronously for 4 months.

### 2.3 Analysis Methods

The output voltage of CW-MFC was measured and recorded by a data acquisition equipment. The specific surface area and the pore size distribution of the filler was indirectly used to characterize the contamination of the filler. The multi-point BET method was used to measure the specific surface area and pore size distribution. The relevant test was carried out by Autosorb-iQ-C automatic physical adsorption instrument. The sample pretreatment temperature was 200 °C.

# **3 Results and Discussion**

# 3.1 Specific Surface Area Analysis of CW and CW-MFC System

According to the adsorption-desorption isotherms of the BET test of CW and CW-MFC systems (shown in figure 2), the relative pressure (P/Po) on the adsorption isotherm was selected among the point of 0.05-0.35 for BET calculation further for the specific surface area. The result showed the specific surface area of the fresh AC was 133.8 m<sup>2</sup>/g, the specific surface area of the filler in CW system was 38.1 m<sup>2</sup>/g, and the specific surface area of the filler in CW-MFC system was 58.2 m<sup>2</sup>/g. The regular activated carbon filler has the largest specific surface area while filler in CW system has the least. The fillers in the CW-MFC system and CW system were different before and after the system operation treatment of the oil production wastewater. The specific surface area of the filler in CW system was reduced by 72%. The specific surface area of the filler in CW-MFC system also showed a decreasing trend, but the degree of decline was lower than that in CW system, only 57%.



**Figure 2.** Adsorption-desorption isotherms of regular activated carbon, CW system and CW-MFC system

### 3.2 Pore Size Distribution and Pore Volume Analysis of the filler in CW and CW-MFC system

The BET analysis software was used to calculate and analyze the pore size distribution and pore volume of the regular activated carbon filler, filler in CW system and CW-MFC system. The results were shown in Figure 3.

The result showed that the pore size of the regular activated carbon filler without any experiment was mostly distributed below 8 nm. The macropores were rare and the pore volume was relatively large while the largest reached 0.14 cm<sup>3</sup>/g. The fillers in CW system and CW-MFC system were all regular activated carbon fillers before the experiment. After the treatment of the oil wastewater for a period of time, the pore size distribution and pore volume of the fillers in CW system and CW-MFC system changed differently. The pore volume of the filler in CW-MFC system was reduced, and the maximum pore volume was 0.08 cm<sup>3</sup>/g. The pore volume of the filler in CW system decreased more, while the maximum pore volume reached  $0.06 \text{ cm}^3/\text{g}$ . The experimental results were consistent with the above conjecture. It had a certain inhibitory effect on the clogging of filler in CW-MFC system due to the existence of micro-electric field of microbial fuel cell.



Figure 3. Pore size distribution of regular activated carbon, filler in CW system and CW-MFC system.

### 3.3 Discussion

The decrease in specific surface area was due to the fact that the contaminants in the wastewater failed to pass through the activated carbon filler, causing the pores to clog, resulting in the decrease in the number of pores, which ultimately caused a decrease in specific surface area. After analysis, we found that the clogging problem of CW-MFC system was reduced compared with the filler in CW system, indicating that the CW-MFC system had a better performance to the clogging of the filler due to the micro electric field of microbial fuel cell.

The size of the specific surface area had an important relationship with the pore size, and they were inversely proportional to each other. It is usually that the specific surface area increases as the pore size decreases. When the CW and CW-MFC systems were used for oil sewage treatment, the materials in the oil wastewater were sure to block and contaminate the filler, so the pore size distribution and specific surface area of the filler would change.

The contamination problem of fillers in constructed wetland has certain similarities to the membrane fouling problem of membrane bioreactors (MBR). They are both related to the growth of suspended solids and microorganisms in sewage. Further studies have shown that if a conductive loop is constructed in the MBR, the electrochemical membrane bioreactor (EMBR) which is composed of the MBR-MFC system can generate self-biasing of the membrane module. It can reduce membrane fouling without consuming external energy. This effect is similar to the applied voltage [10].

The activated carbon filler was used as cathode in the CW-MFC system. The voltage of our reactor came at 260 mV when the reactor operated stably. When the organic materials were consumed at the anode, generated proton shifted from anode to cathode, which could cause a micro electric field. Most suspended solids and bacteria were negative charged and the charged particles and bacteria have the potential to move under the action of the micro-electric field, which may cause changes of cumulative trajectories (Figure 4). The micro-electric field was possible to have a practical effect of reducing the clogging filler. The data obtained in this research were some basic results, some detailed issues deserved to

be further researched.



Figure 4. The movement trajectories of the charged particles with or without the micro electric field

# 4 Conclusions

This study measured and analyzed the specific surface area, pore size distribution and pore volume among the three different material – the regular activated carbon filler, the filler of the CW system and the CW-MFC which had been stably system operated in oil-contaminated wastewater for 4 months. The result showed that the fresh activated carbon filler has the specific surface area of 133.8 m<sup>2</sup>/g while the filler in the CW system has the area of 38.1  $m^2/g$  and the specific surface area of the filler in the CW-MFC system was 58.2 m<sup>2</sup>/g. The surface decrease of the CW-MFC filler was 21% lower than that of CW filler. Comparing with the regular CW, the filler in the CW-MFC was more clogging resistant. It showed that the alleviation of the filler clogging in CW-MFC may be caused by the micro-electric field as the function of MFC. As a promising microbial electrochemical technology for wastewater treatment and filler clogging resistant, CW-MFC may have potential application value.

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