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# Simultaneous pollution treatment and electricity generation of tannery wastewater in air-cathode single chamber MFC

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## ABSTRACT

An innovative bioelectrochemical technology in the form of an air-cathode single chamber microbial fuel cells (SC-MFCs) was utilized to concurrently reduce nitrogen and organic pollutants as well as generate electricity from tannery wastewater under anoxic pH 7 conditions at 37 °C. Subsequent to 4 d semi-batch mode with initial concentrations of soluble chemical oxygen demand (sCOD), total kjeldahl nitrogen (TKN) and ammonia nitrogen  $\text{NH}_4\text{-N}$  of 1,100, 431, and 206.08  $\text{mg L}^{-1}$ , these pollution were diminished by 88, 50 and 35%, respectively. Negligible electricity was created ( $7 \text{ mW m}^{-2}$ ). Removal of the nitrogen pollution in the tannery wastewater occurred in the SC-MFCs was clearly driven by nitrification and denitrification.

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## Introduction

Resulting from a steady and consistent rise in the global population, demand has increased dramatically for fossil fuel use and also resulted in intensified amounts of domestic and industrial wastewaters. Particularly for petroleum, an inevitable energy crisis appears to be approaching as the result of the exhaustion of fossil fuel resources [1]. Due to the chemical

oxygen demand (COD) and nitrogen content involved, which are likely detrimental to the ecosystem, industrial wastewaters are also a significant pollution issue. In order to deal with wastewater before its discharge into the surroundings, suitable technology is needed. Sustainable treatment and utilization of wastewater are receiving intensive attention due to the growing shortage of freshwater resources, and energy crisis. Nowadays, most traditional wastewater treatment

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processes consume energy, cause environmental problems [2], and produce large quantities of excess sludge, which is energy and economically costly for disposal [3]. Microbial fuel cells (MFCs) or bioelectrochemical systems have been received worldwide attention as a new technology of directly generating electricity from organic matter in wastewater [4,5], while simultaneously treating the wastewater. In the MFCs system, much lower energy input is required and much less excess sludge is generated compared with the traditional wastewater processes. MFC reactors are designed for anaerobic treatment by bacteria in the solution near the anode, with the cathode exposed to oxygen (or an alternative chemical electron acceptor). Electrons released by bacterial oxidation of the organic matter are transferred through the external circuit to the cathode where they combine with oxygen to form water. A variety of wastewaters have been successfully treated with simultaneous electricity generation such as brewery wastewater [6], meat processing [7], food processing [8], tannery, paper recycling [9], and municipal wastewaters [10], which have been found to be biocatalysts for directly power generation and waste treatment in MFCs.

Nitrogen-rich wastewater without proper treatment prior to discharge can cause eutrophication that is significantly harmful to waterbodies. MFC is an intriguing device to treat nitrogen compounds since oxic and anoxic environments exist in the MFCs. The recent study has been illustrated MFCs are able to generate electricity; and treat chemical oxygen demand (COD) and nitrogen pollution in wastewaters [7,11–17]. This study employed air cathode SC-MFCs as a device to examine the process of simultaneously reducing carbon and nitrogen pollution; and electricity generation from tannery wastewater. The ability of voltage outputs of the MFC was evaluated. Nitrogen removal and its reduced products in both aqueous solution and gaseous phase were measured.

## Materials and methods

### Wastewater and inoculum

Tannery wastewater was obtained from the effluent of primary settling tank (Ked Prakobkarn Autsahakam Foknang KM. 30 km Co., Ltd., Samut Prakarn province, Thailand). The wastewater was used without sterilization and stored at 4 °C until use. The pH of tannery wastewater was 8.17 and COD: N ratio around 2.5: 1. The pollution load estimated 1100 mg-COD L<sup>-1</sup> and 431 mg TKN L<sup>-1</sup>.

The microbial seed was obtained from full-scale up flow anaerobic sludge blanket (UASB) of cassava starch, Eiamburapa Group Co., Ltd., Srakreaw Province, Thailand. The microbial seed in initial was consisted of *Firmicutes* bacteria (class *Bacillales*) [18]. Coarse matter >0.5 mm diameter was removed by sieving and granules were washed with tap water twice prior to use.

### Enrichment and MFC operation

The SC-MFCs were used to enrich electrochemically active bacteria [19]. Initially, 1 mL (18.18 g TVS) of the inoculum was injected into the SC-MFCs; fed with an artificial wastewater of

500 mg COD L<sup>-1</sup> (COD: N ratio of 4:1) as the electron donor; and operated under mesophilic (37 °C) semi batch mode, pH 7, and an open circuit condition until the SC-MFCs performance reached steady state with respect to pH, potential output and percentage of COD and nitrogen removal. The operation was switched to closed circuit with 1000 and 10 Ω external resistance after the steady state of the open circuit operation. After the closed circuit operation fed with the artificial wastewater reached the steady state, tannery wastewater was fed to the reactor and operated under the same conditions. All experiments were set up in duplicate. During the experiment, total gas composition was periodically monitored. The liquid samples were collected for the measurement of pH, total kjeldahl nitrogen (TKN), ammonia nitrogen (NH<sub>4</sub>-N), COD, and volatile fatty acids (VFAs).

### Chemical analysis, electrochemical and calculation

Standard methods [20] were used for measurement of COD, TKN, and NH<sub>4</sub>-N present in the SC-MFCs. The gas composition and VFAs were analyzed by gas chromatography [18]. Voltage (V) was measured across an external 1000 Ω resistor using a data acquisition system (Keithley 2700 multimeter, USA) and used to calculate the current ( $I = V/R$ ) and power ( $P = IV$ ), where R is external resistance. Columbic efficiency (CE) was calculated by comparing the actual charge produced (integration of current with respect to time) to the available charge, based on the observed COD removal. To calculate the available charge, a conversion factor of 8 g COD/mole electrons (i.e., 4 mol electrons per mole oxygen) was used with Faradays constant (96,485 C/mole of e<sup>-</sup>) to convert electron equivalents to total available charge in Coulombs [7].

Cyclic voltamogram (CV, PGSTAT204, Netherlands) was measured to characterize the oxidation–reduction reaction on electrode surface for electroactive microbial biofilms. The potential was varied from -0.6 to 0.6 V at a scan rate of 20 mV s<sup>-1</sup> while monitoring the current response was using a computer-controlled potentiostat in a three electrode cell consisting of anode as working electrode, cathode as counter and Ag/AgCl (3 M KCl) as reference electrodes.

## Results and discussions

### Enrichment

Potential was stable approximately 0.27 V after 144-h open-circuit operation (Fig. 1A). The SC-MFCs that contained only wastewater did not develop significant potential (data not shown). The open-circuit operation was carried out for one week before it was switched to external loads of 1000 and 10 Ω, respectively (Fig. 1B). At the steady condition, COD was removed approximately 67% (Fig. 2). The close circuit condition with high external resistance (1000 Ω) was connected to obtain more electrochemical bacteria. Low resistance (10 Ω) was used to enhance electron transfer rates within microbial biofilms [21]. After the resistance was connected between the anode and cathode, the voltage was gradually decreased and stable with respect to 85% COD removal after 10 d operation (Fig. 3A, B). These results suggested that the electrochemical

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