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Microbial electrolysis cell to treat hydrothermal liquefied wastewater from cornstalk and recover hydrogen: Degradation of organic compounds and characterization of microbial community

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ABSTRACT

Cornstalk, as an abundant renewable biomass resource, could be used for biocrude oil production through hydrothermal liquefaction (HTL), however, recalcitrant wastewater is released as the main byproduct. This study reported the degradation of recalcitrant wastewater and simultaneous hydrogen production via a continuous up-flow fixed-bed microbial electrolysis cell (MEC). Chemical oxygen demand removal rates were over 60% under different applied voltages and the highest reached 80.2% at 1.2 V. Specifically, GC–MS analysis identified recalcitrant organic matter in HTL wastewater like dimethyl phthalate and diethyl phthalate were significantly removed in a ratio of 95.3% and 79.3% via this MEC. A hydrogen production rate of 3.92 mL/L/d was achieved at 1.0 V in the cathode, whereas the maximum power density (305.02 mW/m^3) was obtained at 0.6 V. Illumina MiSeq sequencing revealed that the content of phylum *Proteobacteria* in anodic biofilm (70.19%) was much higher than the inoculum (20.38%). The dominant genus *Xanthobacter* (58.17%) in anodic biofilm was probably associated with the degradation of dimethyl phthalate. This work suggested that it is feasible to efficiently degrade recalcitrant wastewater from HTL of cornstalk and simultaneously produce hydrogen through MEC.

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Introduction

Hydrogen is a clean and renewable energy carrier, and it has the highest combustion heat in weight of all fuels. Currently, hydrogen is primarily produced via thermochemical processes that consume significant amounts of fossil fuels [1]. However, biohydrogen is a renewable and sustainable approach for hydrogen supply [2,3], which has its specific advantages of broad substrate spectrum and no strict requirement of reaction conditions.

Dark fermentation is the most common method of biohydrogen production by strict or facultative anaerobic bacteria. The theoretical maximum hydrogen yield was 4 mol H_2/mol glucose through dark fermentation [4]. However, this is only one third of the value (12 mol) based on the stoichiometric conversion of glucose to hydrogen. Thus, hydrogen production through dark fermentation inevitably brings out a couple of co-products, such as acetic acid, butyric acid, propionic acid, and ethanol, which cannot be further converted to hydrogen [5]. In comparison, hydrogen production by microbial electrolysis cell (MEC) has its prominent characteristics, such as efficient conversion of feedstock without the limit of thermodynamics, and easy control of hydrogen production [6]. In MECs, the substrate is biologically degraded by microorganism at the anode into CO_2, protons, electrons, and residual organic matter [7]. Microbial biomass and sludge may be also accumulated through assimilation. The bacteria transfer the electrons to the anode and then they are released to the cathode through the circuit [5]. And the protons pass to the cathode across the proton exchange membrane (PEM) or the cation exchange membrane. When protons meet with electrons at the cathode, hydrogen can be generated with applied voltage [8]. MECs can degrade volatile fatty acids (VFAs) in the anode, and simultaneously hydrogen is generated in the cathode of MECs through a small additional power supply. For example, the decomposition reaction of propionate into acetate is thermodynamically unfeasible, and therefore additional power is needed to overcome its energy barrier [9]. The theoretical minimum voltage in acetate fed MEC was only 0.135 V for hydrogen production, much smaller than water electrolysis (1.22 V) [10]. In fact, hydrogen production via MEC was firstly reported from acetate at an applied voltage over 0.25 V [8].

On the other hand, a considerable amount of agricultural residues were generated globally, such as in China (0.7 billion tons/year) [11] and India (0.6 billion tons/year) [12]. However, such waste biomass resources are not well utilized based on the current utilization situations. Thus it has a tremendous potential to utilize various forms of biomass such as cornstalk, sugarcane bagasse, and banana residues for a bio-based industry. The abundant agricultural residues contains renewable energy and carbon resources, which are mainly composed of cellulosic and lignocellulosic materials [13]. Bioelectrochemical system (BES) can utilize a wide range of diverse organic wastes and renewable biomass as substrate. However, cellulosic and lignocellulosic biomass limits the performance of cellulosic and lignocellulosic BES due to their recalcitrant nature for biodegradation [14]. Thus, most studies on BES employed the hydrolyzate of agricultural residues as the substrate.

Hydrothermal liquefaction (HTL), is a thermochemical process, in which biomass is converted into liquid fuels in hot and pressurized water [15]. Recently HTL has received tremendous attention as one of the most promising technologies for biofuel production from different types of wet biomass feedstock, because of a better energy return on investment, lower greenhouse gas emission and higher economic potential [16]. Biocrude oil production from cornstalk via HTL has been recently reported [17,18]. Most researchers focused on the production and properties of biocrude oil, while a large amount of wastewater containing various nutrients is produced as a co-product during HTL. The high concentrations of aqueous organic compounds specifically toxic complex organic substances like N&O-heterocyclic compounds are generally unsuitable to be directly discharged to the environment without additional treatment processing [19,20]. Moreover, amides and N&O-heterocyclic compounds make this kind of wastewater highly recalcitrant to be degraded. At the same time, studies on MECs mainly focused on substrate spectrum [13,21,22], the improvement of hydrogen productivity and treatment capacity of wastewater [21,23,24]. Various recalcitrant wastewater was successfully degraded through MEC, including the fermented corn stover hydrolyzate [25], biorefinery recycle water [26], switchgrass pyrolysis-derived aqueous phase [27], Azo dye wastewater [28], textile wastewater [29], penicillin wastewater [30], molasses wastewater [31], biodiesel waste streams [32], and palm oil mill effluent [29]. In addition, MECs also exhibited a good performance on the treatment of recalcitrant pollutants, such as aniline [33], methyl orange [34], nitrofurans furazolidone [35], furanic and phenolic compounds [36]. However, the conversion of hydrothermal liquefied wastewater from cornstalk through BES has seldom been studied.

In a previous study, we had established a carbon nanotubes (CNTs) fix-bed microbial fuel cell (MFC) for energy production from wastewater. Here, we modified MFC into MEC and focused on the continuous degradation of HTL wastewater from cornstalk and simultaneous hydrogen production via an upflow fix-bed MEC. The specific purposes of this study were 1) to testify the feasibility of simultaneous hydrogen production and degradation of recalcitrant organics via MEC; 2) to investigate the degradability of recalcitrant compounds in HTL wastewater via MEC; 3) to analyze the microbial diversity involved in MEC using Illumina MiSeq sequencing.

Materials and methods

HTL treatment of cornstalk and MEC substrate characteristics

Cornstalk was collected from Golden-sun farm (Beijing, China), and its dry biomass mainly consisted of cellulose (45.06%), hemicellulose (29.68%), and lignin (5.65%). HTL of cornstalk was performed in a 1.8 L batch reactor (Model 4593, Parr Instrument Company, USA) at initial total solid (TS) of 20% [37]. Heating stopped when the temperature reached the set value (312 °C), and the stir speed was set as 300 rpm during the experiment. The HTL products were divided into two phases using vacuum-filtration method. The obtained