Simultaneous sulfide removal and electricity generation with corn stover biomass as co-substrate in microbial fuel cells

Jing Zhang, Baogang Zhang, Caixing Tian, Zhengfang Ye, Ye Liu, Zhongfang Lei, Wenli Huang, Chuanping Feng

Abstract
Microbial fuel cells (MFCs), representing a promising method to treat combined pollutants with energy recovery, were utilized to remove sulfide and recover power with corn stover filtrate (CSF) as the co-substrate in present study. A maximum power density of 744 mW/m² was achieved with sulfide removal of 91% during 72 h operation when the CSF concentrations (mg-COD/l) and the electrolyte conductivity were set at 800 mg/l and 10.06 mS/cm, respectively, while almost 52% COD was removed due to the microbial degradation of CSF to the volatile organic carbons. CSF concentrations and electrolyte conductivities had significant effects on the performance of the MFCs. Simultaneous removals of inorganic pollutants and complex organic compounds with electricity generation in MFCs are reported for the first time. These results provide a good reference for multiple contaminations treatment especially sulfide containing wastewaters based on the MFC technology.

1. Introduction
Combined pollutant in wastewaters is widely produced throughout the world, bringing serious challenges and constrains on conventional wastewater treatments (Starostin and Sorokhtin, 2011; Velvizhi and Mohan, 2011). Sulfide is a typical kind of toxic, corrosive and malodorous pollutant which is commonly found all around the world, particularly in various wastewaters (Omri et al., 2011). It can be treated by physicochemical and biological processes (Zhang et al., 2008; Kumar et al., 2010a), while the coexisted substances in sulfide containing wastewaters may affect the process efficiency. Microbial fuel cells (MFCs) that can recover electrical energy from pollutants with bacteria as catalysts in mere one step (Logan et al., 2006; He et al., 2008; Zhuang et al., 2010; Zhang et al., 2012b), are demonstrated to effectively remove sulfide by oxidizing it to elemental sulfur (Rabaey et al., 2006; Zhang et al., 2009a). However, little attention has been focused on the effects of degradable organics on sulfide removal in MFCs in previous studies (Zhao et al., 2008; Sun et al., 2009). Zhang et al. (2009a) advocate it for the first time that the addition of glucose, which serves as the carbon source of sulfur-relating microbes, has enhanced the performance of the MFCs in electricity generation as well as sulfide removal. Lee et al. (2012) test the excessive application of lactate in MFCs to avoid any carbon limitations on microbes for sulfide removal. These results indicate that MFC technology is an effective method to treat combined pollutants relating sulfide, while only simple organics have been involved in these previous studies. Behaviors of complex organic compounds as well as...
interactions between sulfide and organics should be further investigated due to their competitions as electron donors and associations for pollutants removals in MFCs (Dutta et al., 2010).

In another aspect, organic carbon sources utilized by exoelectrogenic bacteria in MFCs vary from single carbohydrates to complex organics that commonly existed in wastewaters (Clauwaert et al., 2007). Corn stover is a sugar enriched biomass consisting of a mixture of cellulose, hemicelluloses and lignin, and reasonable to be broken down by microbes. Zuo et al. (2006) and Wang et al. (2009) have proved that steam exploded corn stover as the sole electron donor can be utilized by microbes to generate electricity in MFCs, respectively, while these studies are carried out without the consideration of any other co-substrates.

In this study, sulfide-related combined pollutant was explored for the first time, as complex organics of corn stover filtrate (CSF) was employed as co-substrate in MFCs. The performance characteristics of the co-substrate MFCs system, including power output, sulfide removal and corn stover degradation were monitored. Effects of initial CSF concentrations and electrolyte conductivities on power outputs as well as sulfide and corn stover removals were also examined to optimize the operating conditions. Compositions of the initial filtrate and their degradations in the effluents were detected respectively. Effects of CSF on the sulfur-relating exoelectrogenic bacteria activities and sulfide removals were also investigated.

2. Materials and methods

2.1. Construction of MFCs

Four cubic single-chamber MFCs were constructed according to a novel design reported in our previous study (Zhang et al., 2012a), with an effective volume of 125 ml (5 × 5 × 5 cm). The carbon fiber felt anode (1 cm thickness, 4 cm length and width, Beijing Ever Grow Resources Co. Ltd., Beijing, China) was laid in the middle of the chamber. The cathode made of plain carbon paper (with 0.5 mg/cm² of Pt on one side) was placed on the opposite site of the anode, with a projected surface area of 16 cm². The electrodes were connected to the external resistance of 1000 Ω using copper wires with all exposed surfaces sealed with non-conducting silicone. The MFCs were then attached to a data acquisition system (PMD1208LS, Measurement Computing Corp., Norton, MA, USA) to record voltage at an interval of 5 min (Zhang et al., 2009b).

2.2. CSF and electrolyte preparations

Dry corn stover was harvested from a farm in Changping district (Beijing, China) and stored for 1 year. Corn stover was converted into powder (0.5 mm) by crushing and grinding, and then dried at 40 °C for 48 h (Yoo et al., 2011). The corn powder was filtered to collect the organic derivatives, and about 1000 mg/l COD was obtained from the 2.5 g powder washed for three times with 400 ml water. The anode was obtained from the 2.5 g powder washed for three times with water.

2.3. Operation of the MFCs

The MFCs were inoculated with 25 ml anaerobic sludge obtained from an up-flow anaerobic sludge blanket reactor treating high-sulfate wastewater. MFCs were initially domesticated with glucose (800 mg-COD/l) and sulfide (100 mg/l) at the fixed external resistance of 1000 Ω under 30 °C circumstances, with fresh nutrient buffer solution (NBS) mentioned above. The MFCs were operated in 72 h fed-batch mode as most of sulfide was removed within that time. After several batch cycle operations, the system was considered to be under steady-state conditions when the maximum output was reproducible in two or more cycles. Then the substrate was switched to a medium of CSF with NBS as before, and operated for similar maximum voltages in two or more consecutive cycles (72 h for each). When stabilized, experiments were conducted to investigate the effects of different initial CSF concentrations (400, 800, 1200, 1600 mg/l) and electrolyte conductivities (4.85, 7.25, 10.06, 15.27 mS/cm, adjusted by NaCl) on electricity productions and sulfide removals, respectively. The experiments were carried out in duplicate and only the mean values were reported.

2.4. Chemical analytical methods

Measurement of COD was based on digestion with potassium dichromate in concentrated sulfuric acid for 2 h at 150 °C, and sulfide is not counted as a composition of the COD except where stated otherwise. Sulfide was determined according to the methylene blue method (n = 665 nm). The indication of “sulfide” described all species (H₂S, HS⁻, and S²⁻). pH was measured by using a pH meter (Mettler Toledo S02, USA). Electrolyte conductivity was monitored by a conductivity meter (DDS-11A, Shanghai Lei Yun test equipment Manufacturing Co. Ltd., Shanghai, China). Samples were taken at 12 h intervals to measure the residual sulfide, COD, and pH over the course of the whole experiment. Gas chromatography/mass spectrometry (GC/MS) was used to analyze the organic components presented in the CSF influent and the effluent of the MFC system. The CSF of 500 ml was divided into two parts with 250 ml serving as the influent sample and the other 250 ml as the effluent sample after a complete cycle of 72 h in the MFCs. The samples were extracted using 10 ml ethyl acetate for three times and then dried under nitrogen before injected into a 6890 N/5973 GC/MS system (Agilent, USA) equipped with a DB-5 capillary column. The GC process was programmed at 40 °C for 0.5 min, then increased at 10 °C/min to 300 °C, and finally held at isothermal for 10 min. The injector temperature was 250 °C, and the injection size was 1 µl. The flow rate of the carrier gas (helium) was 0.6 ml/min. The ion source temperature was 230 °C for the mass-selective detector (Lei et al., 2009). Analysis was undertaken with reference to the NIST02 mass spectral library database.

2.5. Electrochemical monitoring and data presentations

The MFCs were continuously monitored using a data acquisition system connected to a computer. The circuit was operated under a fixed external load resistance of 1000 Ω except where stated otherwise. The open circuit voltage (OCV) and voltage measurements were taken at 5 min intervals throughout the test. The polarization curves were obtained by measuring voltages at various external resistances (ranging from 10 to 5000 Ω) to evaluate the relationship between voltage and current. For each point on the polarization curves, voltage readings were taken when the voltage stabilized.

To calculate the current (I) in amperes (A) by Ohm’s law, I = U/R, where U is the potential drop in volts (V) across the external load resistor in Ohms. To calculate the power output P in watts (W) and the power density (PD, W/m²) were calculated according to P = I × U and PD = I × U/S respectively, where S (m²) is the geometrical area of the anode. The coulombic efficiency (CE) was deduced as follows, CE = Qf/Qt × 100%, where Qt is the total number of coulombs calculated by integrating the current over time. Qf is the theoretical number of coulombs that can be produced from the used
substrate (expressed in the form total COD containing CSF and sulfide in this study). \( C_T \) was calculated from \( C_T = F b S v T / M_w \), where \( F \) is the Faraday constant (96,485 C/mol), \( b \) is the number of moles of electrons produced per mol of substrate (4 for oxygen), \( S_v \) is the reduction amount of COD, \( v_T \) is the liquid volume in the compartment, and \( M_w \) is the molecular weight of oxygen.

3. Results and discussions

3.1. Start-up of the MFCs

MFCs had been operated for half a year with 750 mg/l glucose and 100 mg/l sulfide at pH of 7 before this present study. During the start-up stage, newly domesticated electrochemical bacteria had a competition with the initial inoculums (Zhang et al., 2009b), and the effective microbial biofilm finally formed on the anode surface. Following stable power generation from glucose and sulfide for several cycle operations, the substrate was switched to the medium containing CSF (800 mg-COD/l) and sulfide (100 mg/l). The MFCs were operated for four cycles to adapt to this new medium. After each cycle of 72 h, addition of fresh nutrients of CSF (indicated by the arrows in Fig. 1) restored the potential to the maximum voltage in the next operating cycle. Power outputs as well as pollutants removal were recorded during this start-up period.

The corresponding voltage output of per cycle with 1000 Ω external resistance totally went through three stages, namely increasing, stable and decreasing period (Fig. 1). During the first cycle, there was a rapid voltage generation reaching 637 mV and stabilized for several hours afterwards. As these organic carbons were consumed and sulfide fully removed, voltage output started to decrease gradually. After 15 days, repeatable cycles of power production were obtained with the maximum voltage output of 725 mV, fully proving the feasibility of electricity generation in the MFCs fed with these combined substrates. It was a little lower than that (823 mV) with glucose and sulfide, due to the relative difficulty to digest macromolecular organics by microbes in MFCs.

Polarization curve was obtained with closed circuit MFCs during a complete cycle period in Fig. 2, after successive stable cycles. A maximum power density of 558 mW/m² was obtained by varying the external resistance. It was much higher than single substrate MFC systems utilizing exploded corn stover hydrolysates or raw corn stover powder with H–C inoculums reported previously (Zuo et al., 2006; Wang et al., 2009). This demonstrated that the co-substrate of CSF was apt to be effectively utilized by microbes for power production. It was also reasoned that sulfide in another way contributed to the high power output, due to its lower electrode potential reducing the anode potential of MFCs. These again indicated that sulfide as well as CSF was suitable electron donors and bacterial nutrition sources in our MFCs.

The sulfide and COD concentrations were monitored at 12 h intervals within a complete operating cycle, achieving the overall removal efficiencies of 81.4% and 51.7%, respectively, with a CE of 15.9% after 72 h operation. The overall CE in our study was a little higher than the previous 12.4% obtained with sulfide and glucose by Zhang et al. (2009a), which was mainly due to the less efficiency in utilizing corn stover by fermentative microbes in MFCs.

3.2. Electricity generations with different initial CSF concentrations and conductivities

In order to investigate whether the initial CSF concentration could be varied so as to improve the MFCs voltage output, a series of experiments were conducted to compare the outputs under different influents (400, 800, 1200 and 1600 mg-COD/l), with sulfide concentration fixed as 100 mg/l. As shown in Fig. 3a, there was directly an ascending trend in the maximum power as the initial CSF concentration went up from 400 to 1600 mg-COD/l. Power outputs increased with the ongoing initial substrate concentrations, in a manner consistent with the Monod kinetics, which was used to describe the bacteria growth tendencies (Natarajan and Suresh Kumar, 2012). The following relationship \( P = P_{max} S / (K_s + S) \) was employed to reveal the ascending trend of the power densities, where \( P_{max} \) (mW/m²) is the maximum power output at a fixed external resistance (1000 Ω), \( S \) is the concentration of wastewater (mg-COD/l) and \( K_s \) is the half-saturation constant (mg-COD/l). As was shown in Fig. 3a, the maximum power density would be obtained as 391 mW/m², with a half-saturation constant of \( K_s = 187 \) mg/l. It was almost 22% higher than the initial 319 mW/m² with the initial 800 mg-COD/l, suggesting that COD concentration would no longer limit the microbial electrochemical activities. Power densities obtained in our co-substrate MFCs system do not fit the Monod-like response so well as those reported in other MFCs with single substrate such as acetate or glucose (Liu et al., 2004), according to the relatively lower \( R^2 \) value of 0.953. This was reasoned that sulfide, serving as an alternative electron donor for electrochemically active microbes in the anode compartment, would make up the insufficiency especially at relatively lower CSF concentrations. Besides, Sun et al. (2009) had proved that electrochemical oxidation of sulfide would take place even without carbon hydrates to generate instantaneous current in the MFCs. However, the gradually declining increase tendency of the power densities at higher CSF

Fig. 1. Voltage outputs of MFCs with CSF as co-substrate for sulfide removal. A straight arrow indicates the addition of fresh substrate.

Fig. 2. Polarization and power density curves of the MFCs with sulfide and CSF as co-substrate.
concentrations suggested that sulfide had hardly affected the system.

MFC reactors fed with mediums under different conductivities were investigated as another approach to increase the power output. Different circuit resistances (10–5000 \( \Omega \)) were used to measure the maximum power densities under different electrolyte conductivities (4.75, 7.25, 10.06 and 15.27 mS/cm). The conductivity of the medium with none NaCl addition was approximate 4.85 mS/cm. When the conductivity went up to 7.25 and 10.06 mS/cm, the maximum power densities increased to 648 and 744 mW/m\(^2\), respectively (Fig. 3b). This phenomenon might be explained that the electron transfer was promoted by additional ions in the solution, hence less ohmic potential loss and accordingly higher power densities (Liu et al., 2005). Moreover, improved biological activities of these anodic microbes might as well result in the final higher power output. However, when the conductivity was further increased to 15.27 mS/cm, a sharp decrease of the maximum power density with the value of 430 mW/m\(^2\) was observed, even 30% lower than 616 mW/m\(^2\) at the initial 4.85 mS/cm. The substantial deterioration in power densities at high conductivity was attributed to the persistent inhibition of high salinity on the electrochemical bacteria (Oh and Logan, 2006). This result was also supported by Zhang et al. (2010), who had reported the similar 16.7 mS/cm to reduce the power generation with the same inoculation in MFCs.

3.3. Sulfide removals with different initial CSF concentrations and conductivities

Effects of CSF concentrations on sulfide removal efficiency were evaluated by varying the initial 400, 800, 1200, 1600 mg-COD/l in the influents, with sulfide concentration fixed at 100 mg/l. Different experiments were conducted as the MFCs were loaded with gradient CSF concentrations, and sulfide concentrations were monitored as a function of time. It could be seen in Fig. 4a that sulfide was generally removed over time except the initial 12 h in a complete operating period. In our present study, microbes on the anode surface were analyzed and species of sulfide oxidizing bacteria and sulfate-reducing bacteria were found, such as Citrobacter sp., Thio- bacillus sp. and Geobacter sulfurreduces, which would be reported in our following research. Thus it could be deduced that fresh sulfide was usually oxidized to sulfur and sometimes even sulfate by sulfide oxidizing bacteria first. Since sulfate would accumulate as the experiment proceeded, it might probably be reduced by these sulfate-reducing bacteria when new medium was added in. As a consequence, the sulfide concentration peaked at the 12 h and then kept gradually descending till the cycle end. The highest sulfide removal efficiency (92%) was achieved at the initial COD concentration of 400 mg/l. While the initial COD concentration went up much higher, the sulfide removal efficiency as well as amount would decrease accordingly. This might due to the competition between CSF and sulfide to serve as electron donors in the MFCs. However, there was not any significant inhibition on sulfide removal when CSF concentration increased (Fig. 4a), indicating that sulfide had predominated in the substrate competition.

Since electrolyte conductivity is a typical factor that would influence the overall performance of MFCs, its influence on the sulfide removal was investigated. Obvious improvements in the sulfide removal efficiencies could be seen in Fig. 4b, when the solution conductivity was increased until the critical 10.06 mS/cm. The maximum sulfide removal efficiency of 91%, 7% higher
3.4. Corn stover degradations during the MFCs operation

Raw corn stover powder was directly filtrated without any sterilization as to immediately serve as the carbon source in the MFCs. The solid weight loss was 1.264 g in the initial 5 g corn stover filtrated by 800 ml water. To further investigate the biological degradations to optimize the MFCs performance.

### Table 1

<table>
<thead>
<tr>
<th>Organic compound name</th>
<th>Formula</th>
<th>Molecular weight</th>
<th>CSF RT (min)</th>
<th>CSF Area (%)</th>
<th>CSF MFC effluent RT (min)</th>
<th>CSF MFC effluent Area (%)</th>
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<tr>
<td>Benzaldehyde, 4-hydroxy-</td>
<td>C6H5O2</td>
<td>122</td>
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<td>12.53a</td>
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<td>12.99</td>
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<td>-</td>
<td>-</td>
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<td>Dimethyl phthalate</td>
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<td>0.25</td>
<td>13.66</td>
<td>1.134</td>
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<td>182</td>
<td>16.15</td>
<td>3.6</td>
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<td>-</td>
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<tr>
<td>6-Methoxy-2-benzoxazolinone</td>
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<td>165</td>
<td>17.43</td>
<td>26.29</td>
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<td>1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester</td>
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<td>278</td>
<td>18.34</td>
<td>6.14</td>
<td>-</td>
<td>-</td>
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<td>2.56</td>
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<td>Di-n-octyl phthalate</td>
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<td>34.89</td>
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<td>-</td>
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<td>Pentanoic acid, 3-methyl-</td>
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<td>Ethane, 1,1,2,2-tetrachloro-</td>
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<td>-</td>
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<td>-</td>
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<td>-</td>
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<td>Hexadecane, 2,6,10,14-tetramethyl-</td>
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<td>Ethyl chloride</td>
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<td>C20H18O4</td>
<td>278</td>
<td>-</td>
<td>-</td>
<td>24.33</td>
<td>22.96</td>
</tr>
</tbody>
</table>

* Values denoted relative percentage of integration area.

a Not detected.

than that obtained at 4.87 mS/cm, was obtained at conductivity of 10.06 mS/cm with 2000 mg/l NaCl. This implied that more soluble ions at high conductivity would promote the electron transfer rate, thus evidently contributing to the sulfide oxidation (Zhang et al., 2010). When more NaCl (4000 mg/l) was added to the reactor, even lower sulfide removal efficiency was obtained as only 79% at conductivity of 15.27 mS/cm. This phenomenon extraordinarily corresponded with the considerable decrease in power densities at the same conductivity. Adverse effect of the much higher conductivity would probably lead to inhibition and inactivation on these electrochemically active microbes (Oh and Logan, 2006), which played important roles in the sulfide removal. Thereby electrolyte conductivity should be reasonably adjusted on the basis of actual situations to optimize the MFCs performance.

The solid weight loss was 1.264 g in the initial 5 g corn stover filtrated by 800 ml water. To further investigate the biological degradations of CSF in the MFC reactors, GC/MS was employed to examine the main organic components in the raw CSF and degradation products in the final MFCs effluent (Table 1). The CSF was mainly composed of various aromatic derivatives (96.61%), which had been previously covered as crackers of cellulose, hemicellulose and lignin in corn stovers (Lei et al., 2009). Aromatic esters (43.83%) were the most abundant compound in both the CSF and effluent, due to the massive ester linkages between cellulose and lignin. The following aldehydes (25.03%) and ketones (26.29%) were most probably the molecular deformations of the ring sugars during the GC process, like glucose, xylose, galactose and so on, which were the usual components of corn stovers as reported before (Zuo et al., 2006). In addition, small amounts of aliphatic hydrocarbons (3.39%) were also observed in initial CSF as a result of chain scissions of the carbon chains on hemicellulose and lignin. However, there was not any furfural detected which are the main hydrolysat of xylose in cellulose and hemicellulose (Yang et al., 2011). It might have volatilized during the vacuum concentration process of ethyl acetate extracts, and the breakup product furan in the effluents would exemplify the furfural existence in the influent (Kumar et al., 2010b). After treated in the MFC system, most of these macromolecular carbohydrates in the filtrate were broken down of small organic molecules.

The most abundant di-n-octyl phthalate (34.89%) in the initial CSF and 1, 2-benzenedicarboxylic acid, mono (2-ethylhexyl) ester (22.96%) in the effluent might probably indicate that di-n-octyl phthalate was finally decomposed to benzenedicarboxylic esters accompanied with chain scissions to short-chain hydrocarbons, alcohols or acids. It was proposed that simple benzenedicarboxylic esters were inedible organics for bacteria in the MFCs, due to a thin representation of 8.69% in the CSF in contrast to the amplifying 26.51% in the effluent. The tiny alternations of dimethyl phthalate and 1,2-benzenedicarboxylic acid bis(2-methylpropyl) ester in the CSF and effluent would also accordingly account for that. Owing to the more vulnerable structure of carbonyl in benzoaldehydes (25.03%), benzoazolinone (26.29%) and propenal (1.46%) to microbes (Yang et al., 2011), they had finally broken into phenols (30%) and phenyl esters (22.8%) abounding in the effluent. Besides, aliphatic hydrocarbons (docosane and eicosane) in the CSF (3.39%) served as another source of small molecular aliphatic derivatives of hydrocarbons, alcohols or acids in the effluent.
In conclusion, most of the organic compounds in CSF could be degraded efficiently to benzene derivatives of small molecule (phenols, phenyl esters and indoles) by microbes in the MFCs. It is likely that these macromolecular components might be firstly degraded by some cellulose or cellulose-digesting bacteria, such as Clostridium clariflavum in our present study. Then the produced soluble fermentation products of benzene derivatives (phenols, phenyl esters and indoles) would probably be further utilized by other exo-electrogenic microbes on the anode. There were still some edible alcohols and acids as well as pyran, which is the fundamental structure of glucose and arabinoise (Patwardhan et al., 2009), for the bacteria in MFCs. This suggested that more sustainable electricity could be collected from the MFCs in accordance with data exhibited in Fig. 1. Besides, cyclic octaatomic sulfur was also presented in the MFCs effluent, implying the generation of elemental sulfur from sulfide oxidation consistent with Zhang et al. (2009a). Further research should be focused on taking full advantage of these complex organics in CSF and optimizing the MFCs system for combined pollutants removals.

4. Conclusions

Successful sulfide removal and power recovery energy with CSF as co-substrate were realized in MFC systems. A maximum power density of 744 mW/m² was achieved with sulfide removal of 91% during 72 h operation when the CSF concentrations and the electrolyte conductivity were set at 800 mg/l and 10.06 mS/cm, respectively. Organics presented in CSF were also degraded accordingly as almost 52% of COD was removed. CSF concentrations and electrolyte conductivities affected the performance of MFCs significantly. Combined pollutants of sulfide and corn stover can be successfully treated in MFCs with renewable and sustainable electricity generation.

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