Technical Note

Electron transfer capacity dependence of quinone-mediated Fe(III) reduction and current generation by Klebsiella pneumoniae L17

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HIGHLIGHTS

- Quinones enhanced goethite reduction and current output by Klebsiella pneumoniae.
- EAC and EDC of synthetic quinones were determined by using chronoamperometry.
- Quinone-mediated electron transfer effectiveness was well correlated with ETC.

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ABSTRACT

Quinone groups in exogenous electron shuttles can accelerate extracellular electron transfer (EET) from bacteria to insoluble terminal electron acceptors, such as Fe(III) oxides and electrodes, which are important in biogeochemical redox processes and microbial electricity generation. However, the relationship between quinone-mediated EET performance and electron-shuttling properties of the quinones remains incompletely characterized. This study investigates the effects of a series of synthetic quinones (SQs) on goethite reduction and current generation by a fermenting bacterium Klebsiella pneumoniae L17. In addition, the voltammetric behavior and electron transfer capacities (ETCs) of SQ, including electron accepting (EAC) and donating (EDC) capacities, is also examined using electrochemical methods. The results showed that SQ can significantly increase both the Fe(III) reduction rates and current outputs of L17. Each tested SQ reversibly accepted and donated electrons as indicated by the cyclic voltammograms. The EAC and EDC results showed that Carmine and Alizarin had low relative capacities of electron transfer, whereas 9,10-anthraquinone-2,6-disulfonic acid (AQDS), 2-hydroxy-1,4-naphthoquinone (2-HNQ), and 5-hydroxy-1,4-naphthoquinone (5-HNQ) showed stronger relative ETC, and 9,10-anthraquinone-2-carboxylic acid (AQC) and 9,10-anthraquinone-2-sulfonic acid (AQS) had high relative ETC. Enhancement of microbial goethite reduction kinetics and current outputs by SQ had a good linear relationship with their ETC, indicating that the effectiveness of quinone-mediated EET may be strongly dependent on the ETC of the quinones. Therefore, the presence of quinone compounds and fermenting microorganisms may increase the diversity of microbial populations that contribute to element transformation in natural environments. Moreover, ETC determination of different SQ would help to evaluate their performance for microbial EET under anoxic conditions.

1. Introduction

Exogenous electron shuttles (ESs) can facilitate extracellular electron transfer (EET) from the bacterial cell surface to insoluble terminal electron acceptors (e.g., iron(III) oxides), resulting in significant enhancement of microbial dissimilatory iron reduction under anaerobic conditions (Watanabe et al., 2009; Roden et al., 2010). Some ES have also been used to enhance microbial electricity generation in microbial fuel cells (MFCs) (Thygesen et al., 2009). Quinone groups in ES function as a recyclable mediator during the electron transfer process, in which the quinones are microbiologically reduced to hydroquinones, and then these hydroquinones are again oxidized by terminal electron acceptors to the corresponding quinones (Scott et al., 1998; Lovley et al., 2004; Brose and James, 2010). A strong relationship was found between redox potentials of ES and their enhanced Fe(II) production during lepidocrocite reduction by Shewanella putrefaciens (O’Loughlin, 2008). However, the redox potentials of most active quinones fall in a narrow range of −137 to −225 mV (vs. SHE at pH 7) for enhancing ferricydrate
reduction by Geobacter metallireducens (Wolf et al., 2009). The effectiveness of ES for Fe(III) oxide reduction is largely influenced by various experimental conditions, e.g., species of bacteria, electron donors, and ES concentrations and redox properties. Most studies that have examined ES enhancement of EET from bacteria to insoluble electron acceptors focused on dissimilatory iron-reducing bacteria (DIRB), mainly species of Geobacter and Shewanella (Burgos et al., 2003; Lovley et al., 2004; Liu et al., 2007; O’Loughlin, 2008; Wolf et al., 2009). However, a phylogenetically diverse range of bacteria not primarily classified as DIRB (e.g., some fermenting, sulfate-reducing, and methanogenic bacteria), can also use ES as an electron acceptor for the anaerobic oxidation of organic and inorganic electron donors (Benz et al., 1998; Cervantes et al., 2002; Field and Cervantes, 2005; Li et al., 2009). Furthermore, the abundance of fermentative bacteria is usually one or two orders of magnitude higher than DIRB in iron-bearing environments (Reiche et al., 2008); however, few studies have considered effects of ES on Fe(III) oxide reduction by fermenting bacteria.

The role of quinone-hydroquinone moieties as redox mediators has drawn considerable interest in the investigation of their electron-shuttling properties. Recently, chemical, biochemical, and electrochemical approaches have been successfully employed to evaluate the electron transfer capacities (ETCs), i.e., electron acceptor (EAC) and donor (EDC) capacitances of quinones, humic acids, and dissolved organic matter from aquifers, soils, and sediments (Blo
dau et al., 2009; Aeschbacher et al., 2010, 2011; Yuan et al., 2011). However, limited information is available on the association between EAC/EDC and ES-mediated EET performance.

Using a fermentative bacterium, Klebsiella pneumoniae L17, which has iron-/huminic-reducing and current generation abilities (Zhang et al., 2008; Li et al., 2009; Liu et al., 2011a), this study aims to (i) investigate the effects of seven SQ on microbial goethite reduction and current generation, (ii) evaluate the electron-shuttling properties of SQ, i.e., voltammetric behavior, EAC, and EDC, using electrochemical approaches, and (iii) discuss the relationship of redox potentials and ETC on their effectiveness for microbial goethite reduction and current generation, respectively. This study is expected to provide meaningful information to understand the correlation of the electron-shuttling properties of quinones with their ability to mediate EET by fermenting bacteria.

2. Materials and methods

2.1. Materials

Klebsiella pneumoniae L17 was isolated previously from subtropical forest sediment in Zhaqing, China. Goethite (α-FeOOH) was synthesized as described previously (Li et al., 2009). Carmine (Car, >97%), 9,10-anthraquinone-2-carboxylic acid (AQC, 98%), 2-hydroxy-1,4-naphthoquinone (2-HNQ, 97%), and 5-hydroxy-1,4-naphthoquinone (5-HNQ, 97%) were purchased from Sigma–Aldrich (USA). Alizarin (Ali, 97%), 9,10-anthraquinone-2-sulfonic acid (AQS, >98%), and 9,10-anthraquinone-2,6-disulfonic acid (AQDS, >98.0%) were purchased from Fluka (Japan). Other chemicals were of analytical grade and obtained from Guangzhou Chemical Co. (China). Individual stock solutions (10 mM) of AQS and AQDS were prepared in water and filter-sterilized (0.22 μm); stock solutions of 2-HNQ and 5-HNQ were prepared in methanol; and those of AQC, Ali, and Car were prepared in acetone.

2.2. Fe(III) reduction experiment

The medium contained the following components (per liter of deionized H2O): NaHCO3, 2.5 g; NH4Cl, 0.25 g; Na2HPO4·2H2O, 0.68 g; KCl, 0.10 g; mineral solution, 10 mL; and vitamin solution, 10 mL (Li et al., 2009). The concentration of glucose as carbon source, α-FeOOH as electron acceptor, individual SQ as electron shuttle, and cells of K. pneumoniae L17 after being added into the medium was 5 mM, 30 mM, 0.1 mM, and 1.3 × 106 cells mL−1, respectively. Cells were harvested as described previously (Li et al., 2009). All anaerobic media were boiled and cooled under a constant stream of 80% N2–20% CO2, dispensed into aluminum-sealed culture bottles under the same gas phase, capped with butyl rubber stoppers, and sterilized by autoclaving (121 °C and 20 min). In addition, inoculation and sampling were conducted using sterile syringes and needles. All experiments were conducted in duplicate. All vials were incubated in a Bactron Anaerobic/Environmental Chamber II with O2 concentration <0.01% (Shellab, Sheldon Manufacturing Inc., Cornelius, OR) at 30 °C in the dark. Fe(II) concentration, as HCl-extractable Fe(II), was determined by extracting Fe(II) from the suspensions using 0.5 M of HCl for 1.5 h and assaying the extract using 1,10-phenanthroline colorimetry, which was not affected by the presence of the tested SQ (Li et al., 2009).

2.3. Current generation experiment

Current generation was tested using a MFC reactor that consisted of two identical chambers separated by a cation exchange membrane (Electrolytica Corporation); each cell chamber had an effective volume of 75 mL. Both electrodes were made of carbon felt (4.5 cm × 4.5 cm each, Panex 33 160 K, Zoltek) and set at the bottom of the chamber. Titanium wire was inserted inside the carbon felt to connect the circuit. A suspension of L17 harvested cells (ca. 107 cells mL−1) and/or SQ (0.1 mM) in a phosphate buffer solution (0.1 M, pH = 7.0) containing glucose (15 mM) was added into the anode chamber under an oxygen-free N2 atmosphere in the Bactron Anaerobic/Environmental Chamber. After the anode chambers of the reactors were sealed with butyl rubber stoppers, the reactors were taken out and the same buffer solution containing 0.2 M potassium ferricyanide as catholyte was added to the cathode chamber under atmospheric pressure. All experiments were conducted at a controlled temperature of 30 °C. A 1000 Ω resistor was used as an external load, and cell voltages were recorded using a 16-channel voltage collection instrument (AD8223, China).

2.4. Electrochemical measurement

Electrochemical experiments were performed using a potentiostat (CHI660D, Chenhua Co. Ltd., Shanghai, China) with a conventional three-electrode cell at ambient temperature (Yuan et al., 2011). A platinum mesh (4 cm × 4 cm) and saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. The working electrode was a glassy carbon electrode (2 mm diameter, MF-2012, BAS) and a graphite plate (3.5 cm × 5.0 cm) for cyclic voltammetry (CV) and chronoamperometry (CA) measurement, respectively. CV measurements were carried out in a phosphate buffer solution (0.1 M, pH = 7.0) in a potential range of −1.2 V to +0.4 V (vs. SCE), with a scan rate of 50 mV s−1. CA measurements were performed in a phosphate buffer solution (0.1 M, pH = 7.0) with 0.1 M KCl as electrolyte at applied potentials of −0.8 and +0.5 V to evaluate the EDC and EAC of the SQ under constant stirring. All solutions were purged with oxygen-free N2 for 15 min before the electrochemical measurements. The final concentration of SQ in the CV and CA measurement was 6.7 μM, with which only the dissolved fraction is present (Wolf et al., 2009); therefore, the redox behaviors and electron transfer capacities were not influenced by the solubility of SQ. In addition, no significant influence was observed for the microbial Fe(III) reduction, current generation, and electrochemical characteristics, when all the experiments and measurements were conducted with addition of an equivalent amount of methanol or acetone without SQ.
3. Results

3.1. Effects of SQ on Fe(III) reduction by L17

The bioreduction of goethite by *K. pneumoniae* L17 with time in the absence and presence of seven SQ is shown in Fig. 1a. The Fe(II) concentrations increased with time; however, only 0.426 mM of Fe(II) was detected in the vials inoculated with L17 but without SQ at the end of the incubation (day 15). Compared with the L17 system, significantly higher Fe(II) concentrations were observed in the vials with the addition of all the examined SQ during the incubation period. The experiment of L17 + AQC showed 4.5-fold higher Fe(II) production than L17 at the end of incubation.

For better comparison of the individual experiments, reaction rates of Fe(III) reduction (k) were calculated by linear regression of the Fe(II) production data from day 0 to day 15 (Li et al., 2009; Wolf et al., 2009; Liu et al., 2011a). Different rates of Fe(II) production by L17 were observed with different SQ (Table 1). Some quinones (i.e., AQC, AQS, AQDS, and 2-HNQ) showed strong accelerating effects; among which, AQC increased the Fe(III) reduction rate of L17 by sevenfold. Other quinones (i.e., Ali and 5-HNQ) showed only small effects, whereas no significant effect on iron reduction kinetics was observed for Car. The results indicate that L17 can weakly reduce α-FeOOH to Fe(II) under anoxic conditions, which is consistent with our previous studies (Li et al., 2009; Liu et al., 2011a). Moreover, the presence of most SQ can significantly increase the extents and rates of Fe(III) reduction by L17.

3.2. Effects of SQ on current generation by L17

*K. pneumoniae* L17 can directly transfer electron to the anode in a MFC for electricity production by utilizing glucose as the carbon source. In this study, MFC reactors inoculated with L17 started to produce electricity after approximately 4 h (data not shown), and constant current generation ranging from 0.157 mA to 0.169 mA in different reactors, was observed after 25 h of incubation, as shown in Fig. 1b and Table 1.

Individually tested SQ was added into the L17 suspension in the anodic chamber of each reactor at 29 h. The current outputs increased immediately with the addition of AQC, AQS, and 2-HNQ, and reached their constant output within 1 h, whereas the current output with AQDS started to increase significantly after 1 h and resulted in an output level similar to that of AQS after 3 h. Although the current output initially decreased with the addition of 5-HNQ, Ali, and Car, it started to increase within 10 min and reached constant output after approximately 2 h. These results show large differences among the tested SQ for facilitating microbial electricity production.

The ratios between constant current outputs before and after the addition of different quinones were applied for better comparison of their effectiveness for microbial electricity production by L17 (Table 1). Most of the investigated SQ showed significant enhancement of current production with the ratios of $I_{\text{L17+SQ}}/I_{\text{L17}}$ ranking as AQC > AQDS > AQS > Ali > 2-HNQ. However, 5-HNQ had merely a small positive effect, and Car even appeared to inhibit microbial current generation by L17.

3.3. Voltammetric behavior of SQ

The electron transfer properties of ES are ascribed primarily to the quinone moieties, the redox behavior of which can be investigated using the cyclic voltammograms (CVs). The major features of the CVs of tested SQ are shown in Fig. 2a. Obvious oxidation-reduction peaks appeared in the CVs of all SQ, indicating that the

![Fig. 1. (a) Concentration of 0.5 M HCl extractable Fe(II) during the bioreduction of 30 mM of goethite by *K. pneumoniae* L17, provided with 5 mM of glucose in the presence and absence of 0.1 mM SQ. Lines are a visual aid only. Data are mean ± SD (n = 3). (b) Current outputs by *K. pneumoniae* L17 in the MFC reactors, provided with 15 mM of glucose in the presence and absence of 0.1 mM SQ.](image)

Table 1

<table>
<thead>
<tr>
<th>Synthetic quinones (SQs)</th>
<th>Fe(III) reduction (k) (mM d⁻¹)</th>
<th>Fe(III) reduction (k) (mM d⁻¹)</th>
<th>Constant current outputs $I_{\text{average}}$ (mA)</th>
<th>$I_{\text{L17+SQ}}/I_{\text{L17}}$</th>
<th>$E_\text{q}$ (vs. SHE, pH 7) (mV)</th>
</tr>
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<tbody>
<tr>
<td>AQC</td>
<td>0.205 ± 0.008</td>
<td>0.566</td>
<td>0.160 ± 0.004</td>
<td>0.275 ± 0.001</td>
<td>1.632</td>
</tr>
<tr>
<td>AQS</td>
<td>0.142 ± 0.003</td>
<td>0.776</td>
<td>0.169 ± 0.003</td>
<td>0.251 ± 0.004</td>
<td>1.416</td>
</tr>
<tr>
<td>AQDS</td>
<td>0.086 ± 0.002</td>
<td>0.671</td>
<td>0.157 ± 0.003</td>
<td>0.246 ± 0.001</td>
<td>1.516</td>
</tr>
<tr>
<td>2-HNQ</td>
<td>0.083 ± 0.005</td>
<td>0.904</td>
<td>0.165 ± 0.001</td>
<td>0.207 ± 0.001</td>
<td>1.256</td>
</tr>
<tr>
<td>5-HNQ</td>
<td>0.035 ± 0.001</td>
<td>0.813</td>
<td>0.161 ± 0.001</td>
<td>0.174 ± 0.003</td>
<td>1.108</td>
</tr>
<tr>
<td>Ali</td>
<td>0.022 ± 0.002</td>
<td>0.887</td>
<td>0.169 ± 0.001</td>
<td>0.224 ± 0.002</td>
<td>1.333</td>
</tr>
<tr>
<td>Car</td>
<td>0.031 ± 0.001</td>
<td>0.947</td>
<td>0.159 ± 0.005</td>
<td>0.152 ± 0.004</td>
<td>0.968</td>
</tr>
<tr>
<td>No SQ</td>
<td>0.029 ± 0.001</td>
<td>0.945</td>
<td>−</td>
<td>−</td>
<td>1.000</td>
</tr>
</tbody>
</table>

* *Wolf et al. (2009)*
quinone moieties in SQ are capable of reversibly accepting and donating electrons. However, the positions and intensities of the oxidation or reduction peaks varied. For example, the positions of the reduction peaks ranged from negative to positive as follows: Car < Ali < AQC < AQDS < 2-HNQ < AQS < 5-HNQ, which is similar to their ranking based on redox potentials $E_0$ (vs. SHE) in the literature (Wolf et al., 2009). Interestingly, a different order was obtained with the intensities of the reduction peaks as: Car < 2-HNQ < Ali < 5-HNQ < AQDS < AQS < AQC. Although all tested SQ have two quinone molecules, they have different structural properties (e.g., number of aromatic molecules) and substitutions of other functional groups (e.g., sulfonic, carboxylic, and phenolic moieties), which may affect their voltammetric behavior.

3.4. Electron transfer capacities of SQ

The tested SQ were first reduced at a potential of $-0.8$ V (vs. SCE) and subsequently oxidized at a potential of $+0.5$ V (vs. SCE) using chronoamperometry to investigate EAC and EDC. In three continuous cycles, AQC acquired the highest EAC and EDC values at 487.8 mmol_–(mol_{SQ})$^{-1}$ and 248.8 mmol_–(mol_{SQ})$^{-1}$, respectively, whereas Car achieved the lowest at 19.01 mmol_–(mol_{Car})$^{-1}$ of EAC and 12.41 mmol_–(mol_{Car})$^{-1}$ of EDC (Fig. 2b). The EAC and EDC were 379.8 mmol_–(mol_{AQC})$^{-1}$ and 361.4 mmol_–(mol_{AQC})$^{-1}$ for AQS, and 248.8 mmol_–(mol_{AQDS})$^{-1}$ and 233.4 mmol_–(mol_{AQDS})$^{-1}$ for AQDS, respectively. Both 2-HNQ and 5-HNQ resulted in similar levels of both EAC and EDC ranging from 132.3 mmol_–(mol_{HNQ})$^{-1}$ to 164.4 mmol_–(mol_{HNQ})$^{-1}$. Ali showed relatively low EAC as 52.42 mmol_–(mol_{Ali})$^{-1}$ and EDC as 42.84 mmol_–(mol_{Ali})$^{-1}$. In addition, individual SQ exhibited a higher EAC value than that of its EDC, which is similar to the results of previous studies (Ratasuk and Nanny, 2007; Bauer and Kappler, 2009; Yuan et al., 2011). Hence, electron transfer in the tested SQ was reversible, and Car and Ali showed relatively low capacities of electron transfer. Meanwhile, AQDS, 2-HNQ, and 5-HNQ showed stronger relative ETC, and AQC and AQS had high relative ones.

4. Discussion

Microbial iron reduction is accelerated by AQDS and other quinones, as aforementioned. The factors influencing the effectiveness of quinones for enhancing iron reduction included bacterial species, quinone concentration, and the redox potential of the quinones (O’Loughlin, 2008; Li et al., 2009; Wolf et al., 2009).

Since some SQ (e.g., 5-HNQ, Ali and Car) have low solubility and high relative adsorption on iron oxide surface (Wolf et al., 2009), the tested SQ introduced from the stock solutions may precipitate or adsorb to different extents, leading to dissolved concentration of less than 0.1 mM. It is well-known that most humic substances in soils and sediments are in particulate, rather than dissolved form, and some iron-reducing bacteria have been demonstrated to be capable of transferring electrons to solid-phase humic substances, resulting in significantly accelerated Fe(III) oxide reduction (Roden...
et al., 2010). In the Fe(III) reduction and current generation experiment, the goethite and electrode was set at the bottom of the serum bottle and reactor’s chamber, respectively. The L17 cells and SQ can simultaneously dissolve in the reaction solution and attach to the surface of goethite and electrode, and both dissolved and solid-phase quinones are considered to be capable of mediating extracellular electron transfer from L17 to goethite and electrode.

4.1. Relationship with redox potentials of SQ

The Fe(II) production rate during lepidocrocite reduction by *S. putrefaciens* with different ES correlated well with their reduction potentials when ES have redox potential values ranging from ~254 mV to +11 mV (O’Loughlin, 2008). Plotting the ratio of Fe(III) to C0 potentials when ES have redox potential values ranging from putrefaciens with different ES correlated well with their reduction et al., 2010). In the Fe(III) reduction and current generation experiment, the goethite and electrode was set at the bottom of the serum bottle and reactor’s chamber, respectively. The L17 cells and SQ can simultaneously dissolve in the reaction solution and attach to the surface of goethite and electrode, and both dissolved and solid-phase quinones are considered to be capable of mediating extracellular electron transfer from L17 to goethite and electrode.

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transferred from ES to iron compounds is indirect, time consuming, and pH-dependent, and may result in different equilibrium values, thereby making it difficult for comparison among datasets (Aeschbacher et al., 2010, 2011; Yuan et al., 2011). Likewise, the SQ-mediated goethite reduction by L17 in this study cannot be used to quantify the number of electrons transferred from SQ to the Fe(III) oxide, but can show the effectiveness of SQ for microbial Fe(III) oxide reduction. However, the EAC and EDC of different SQ determined in this study may be used to assess their ETC in the following procedure.

When the ratios of $k_{\text{L17-SQ}}/k_{\text{L17}}$ were plotted vs. the EAC (Fig. 4a) and EDC values (Fig. 4b) of quinones, $k_{\text{L17-SQ}}/k_{\text{L17}}$ well correlated with both EAC and EDC; as indicated by the high correlation coefficient ($R$) of 0.933 and 0.944 for linear regression fitting for EAC and EDC, respectively. The ratios of $k_{\text{L17-SQ}}/k_{\text{L17}}$ for microbial current generation showed similar correlation with EAC (Fig. 4c) and EDC (Fig. 4d), with correlation coefficients of 0.801 and 0.815, respectively. The effectiveness of different SQ for enhancing Fe(III) reduction and current generation by L17 are positively associated with their EAC and EDC. The redox potential of Ali (−344 mV) is close to the lowest value of c-Cyt (−400 mV), suggesting, thermodynamically, that just a few types of c-Cyt with redox potential lower than −344 mV could reduce Ali. In addition, Ali has a relatively low capacity for electron transfer (Fig. 4b). These factors may explain the relatively modest effectiveness of Ali for microbial Fe(III) reduction and current generation. This result implies that the electron-shuttling property of quinones may not only be thermodynamically controlled by the redox potential, as previously reported (Wolf et al., 2009), but also dynamically controlled by ETC.

4.3. Environmental significance

A number of SQ and humic substances have been reported to play an important role in many redox reactions involved in contaminant transformations and biogeochemical cycling of redox active elements, particularly in anaerobic and anoxic environments (Borch et al., 2010; Brose and James, 2010). In this study, the presence of exogenous SQ facilitated electron transfer to Fe(III) oxide and to an electrode (i.e., current generation) by a fermentative bacterium that is not typically classified as a DIRB. The ubiquity of quinone compounds and fermenting microorganisms in soils and sediments infers that their presence in natural environments or their introduction into contaminated sites may increase the diversity of microbial populations participating in contaminant remediation and element transformation.

Recently, increasing interest has been generated in determining the ETC of ES to evaluate their potential performance of electron shuttling (Blodau et al., 2009; Huang et al., 2010; Aeschbacher et al., 2012a,b). Using the electrochemical approach to investigate the EAC and EDC of different quinones, the effectiveness of quinone-mediated microbial Fe(III) reduction and current generation was shown to be strongly dependent on their EAC and EDC. Therefore, determining the ETC of different ES would be a useful approach to quantitatively estimate their performance for microbial EET acceleration processes, e.g., metal oxide reduction (Lovley et al., 2004; Brose and James, 2010), electricity generation (Thygesen et al., 2009; Watanabe et al., 2009), organic pollutant transformation (Field and Cervantes, 2005; Aeschbacher et al., 2012a) and others.

5. Conclusions

The current study found that the presence of different SQ can significantly increase both the Fe(III) reduction rates and current outputs of a fermenting bacterium, K. pneumoniae L17. CVs indicated that all tested SQ were capable of accepting and donating electrons reversibly. The EAC and EDC determined using chronoamperometry showed that Car and Ali had low relative capacities of electron transfer, whereas AQDS, 2-HNQ, and 5-HNQ showed stronger relative ETCs, and AQ and AQS had high relative ones. Moreover, the effectiveness of different SQ for microbial Fe(III) reduction and current generation was positively correlated with their EAC and EDC.

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