



## Quinone-Mediated Electrochemical Reduction of Ferrihydrite: Effect of Sorption and Redox Potential

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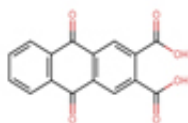
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Natural Organic Matter (NOM) shows both oxidizing and reducing capabilities through its quinone/hydroquinone functional groups and takes part in various geochemically redox reactions. Here four natural and synthetic quinone model compounds (anthraquinone-2,6-disulfonate, AQDS; anthraquinone-2-sulfonate, AQS; 2-hydroxyl-1,4-naphthoquinone, Lawsone; and anthraquinone-2,3-dicarboxylic acid, AQDC) were used to study the effect of adsorption of redox active organic matter on mediating ferrihydrite reduction. The studied quinone compounds varied regarding reduction potential and their tendency to adsorb at ferrihydrite. An electrochemical setup rather than iron reducing bacteria was used to circumvent potential inhibitory effects of the model quinones on microbial activity. Iron speciation, dissolved and adsorbed quinone concentrations and their redox state were monitored to elucidate controlling factors in mediated ferrihydrite reduction. Results show that all model quinones present at 100  $\mu\text{M}$  total concentration enhanced the initial iron reduction rate of ferrihydrite, however, to very different extents. At -0.45 V (vs. Ag/AgCl) redox potential applied, the initial reduction rates increased compared to quinone free systems by factors of 62.53, 43.11, 32.26 and 2.91 for AQDS, AQS, Lawsone and AQDC, respectively. In contrast to AQDC and Lawsone, AQDS and AQS did not show significant adsorption at ferrihydrite under the conditions of our study. Due to the high sorption, the initial dissolved AQDC concentration was only 3.60  $\mu\text{M}$ . The initial dissolved concentration of Lawsone was 85.70  $\mu\text{M}$  and decreased further during ferrihydrite reduction. Adsorbed Fe(II) promoted the adsorption of Lawsone on ferrihydrite thereby decreasing the rate of iron reduction. Our findings demonstrate that the rate of ferrihydrite reduction correlated with dissolved quinone concentrations. As a result, AQDS and AQS showed the highest acceleration of ferrihydrite reduction. At the redox conditions applied (-0.45 V vs. Ag/AgCl) the fraction of reduced quinone species was higher for AQDS than for AQS, consistent with the higher efficiency of AQDS in mediating ferrihydrite reduction.

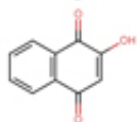
The possibility of conducting experiments at defined redox potentials and precisely controllable experimental conditions reveals the perspectives of an electrochemical setup for the investigation of biogeochemical redox reactions.

**Sorbing quinones:**

Anthraquinone-2,3-dicarboxylic acid (AQDC)

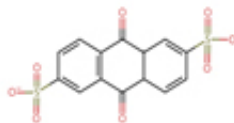


2-Hydroxy-1,4-naphthoquinone (Lawsone)



**Non-sorbing quinones:**

Anthraquinone-2,6-disulfonate (AQDS)



Anthraquinone-2-sulfonate (AQS)

