Electron Transfer Processes Between Hydroquinone and Iron Oxides

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Abstract: The kinetics of hydroquinone oxidation by aqueous suspensions of pure hematite and goethite-ferrihydrite mixtures at pH 6.0, 7.4, and 9 was studied using an on-line analysis system. The electron transfer between hydroquinone and the Fe oxides was monitored by UV-visible and electron spin resonance spectroscopy. The adsorption of organics on the Fe oxide surface was detected by Fourier-transform infrared spectroscopy. For different Fe oxides, a higher surface area was correlated with a greater oxidizing ability and greater adsorption of organics, suggesting that the oxidation reaction was a surface process. A reversal of the initially rapid redox reaction was found in this system, suggesting a delayed release of Fe²⁺ into solution as the reduction of the Fe oxide proceeded. Redox potential calculations confirmed the thermodynamic favorability of the reaction reversal. A distribution of the reduced state over neighboring Fe atoms on the oxide surface probably was responsible for the initial suppression of Fe²⁺ release into the aqueous phase. Based upon these observations and detection of the semiquinone radical as an intermediate of hydroquinone oxidation, an inner-sphere one-electron transfer mechanism for the oxidation of hydroquinone at the oxide surface is proposed.

Key Words: Electron spin resonance • Electron transfer • Ferrihydrite • Goethite • Hematite • Hydroquinone • Iron

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