

Arsenic oxidation by flavin-derived reactive species under oxic and anoxic conditions

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In a variety of natural environments, flavins of microbial origin are a prevalent class of redox-active compounds capable of producing reactive oxygen ($O_2^{\cdot-}$, $\cdot OH$, H_2O_2) and riboflavin (RBFH \cdot) species [1], while also affecting redox conditions and redox potential measurements [2, 3]. This study set out to assess the ability of flavins to stimulate the oxidation of environmental contaminants. In particular, we hypothesized that reduced flavin exudates may be a natural source of efficient oxidants for arsenic (As) remediation under both oxic and anoxic conditions.

Results of batch experiments of 50 min duration performed at 23 °C and in the dark indicate that the extent of As(III) co-oxidation with reduced riboflavin (RBFH $_2$) by O_2 is pH dependent, with a faster reaction rate under mildly acidic (pH 5) than alkaline (pH 9) conditions. Additional quencher tests using 2-propanol (for $\cdot OH$) and catalase (for H_2O_2) indicate that As(III) oxidation is mainly driven by flavin-derived $\cdot OH$ at pH 5 - 7, and by H_2O_2 at higher pH. Kinetic modelling using the Kintecus software [4] further supports two plausible mechanisms of flavin-derived $\cdot OH$ formation: (1) $\cdot OH$ generated from the one-electron reduction of riboflavin-hydroperoxide (RBFHOOH), and (2) $\cdot OH$ formed during the oxidation of (half-)reduced flavin species by H_2O_2 . The kinetic model also reproduces the observed As(III) oxidation by riboflavin radical (RBFH \cdot) generated from co-existing oxidized and reduced riboflavin species under anoxic conditions.

Overall, our study demonstrates that flavins could facilitate As(III) oxidation during environmental bioremediation. We further speculate that flavins may serve as effective oxidant sources for other redox-sensitive contaminants, radionuclides and organic pollutants.

[1] Massey (1994) *J. Biol. Chem.* **269**, 22459-22462.

[2] Monteverde *et al.* (2018) *ES&T* **52**, 12265-12274.

[3] Markelova *et al.* (2017) *Environ. Chem.* **14**, 515-524.

[4] Ianni (2017) Kintecus, Windows Version 6.01, www.kintecus.com.