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Iron speciation and iron species transformation in activated sludge membrane bioreactors

*Xiao-Mao Wang, T. David Waite**

School of Civil and Environmental Engineering, The University of New South Wales, Sydney, NSW 2052, Australia

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ABSTRACT

Iron speciation and iron species transformation were investigated in three membrane bioreactors (MBRs) differing in feed iron concentration (and oxidation state) and the presence or absence of an anoxic chamber to simulate various feed stream conditions and operational configurations. The concentration of dissolved Fe(II) was below detection limit (i.e., <0.1 μM) in all chambers while the concentration of dissolved Fe(III) was found to be around 0.25 μM. H_2O_2 was detected as a quasi-stable reactive oxygen species with concentrations in the μM range in all MBR chambers. H_2O_2 acted as the primary potential oxidant of Fe(II) in the anoxic chamber. Batch experiments showed that the rate constant for oxygenation of dissolved Fe(II) in the liquid phase of the activated sludge compartment was as high as 78 $M^{-1} s^{-1}$. The half-life time of dissolved Fe(II) in all chambers was found to be no longer than 1 min. The stability constants of the Fe(III)SMP complexes were far from uniform. A large quantity of Fe(II) (over 0.036% of the sludge dry mass) was found to be adsorbed by the bacterial flocs suggesting the active reduction of adsorbed Fe(III). The content of adsorbed Fe(II) was found to increase if the MBR was supplied with iron in the Fe(II) form. Over 60% of iron fed to the reactors was converted to highly insoluble ferric oxyhydroxide in all MBRs. A model has been developed which satisfactorily describes the oxidation of Fe(II) in the activated sludge liquid phase and which provides valuable insight into the relative importance of redox processes occurring which mediate the speciation of iron in the system.

1. Introduction

Compared with that in natural systems, iron biogeochemistry in engineered biological systems is seldom studied. The shortage of investigations is no doubt a result, in part at least, of the complexity of the transformations between iron species that may occur and also possibly a result of a lack of appreciation of the critical role that iron plays in engineered biological systems. In actuality, iron is among the most essential trace nutrients for all microorganisms in both natural and engineered biological systems (Stumm and Morgan, 1996). Although the total iron concentration in engineered biological systems is much higher (e.g., typically over 100 μM in feed streams to activated sludge treatment plants (Morel et al., 1975)) than in many natural systems (e.g., concentrations of 0.1–9 nM are typical of marine systems (Hunter and Turner, 2001)), the concentration of iron in solution and available for biological uptake is likely to be similar since, in both instances, under oxic conditions at circumneutral pH values, the thermodynamically favoured ferric iron (Fe(III) is highly insoluble with the concentration of dissolved inorganic Fe(III) species on the order of 10^{-11} M (Morel and Hering, 1993)). Such

* *Corresponding author.*
E-mail address: d.waite@unsw.edu.au (T.D. Waite).
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low concentrations of dissolved iron may limit bacterial growth (or, at least, influence the bacterial species that dominate the biomass) (Chang et al., 1992; Sterner et al., 2004). It is also recognised that stress induced by iron-limitation can result in increased exudation of polymeric materials (Evans et al., 1994), possibly with implications to membrane fouling.

The solubility (and potentially the bioavailability) of iron can be increased by either formation of dissolved Fe(III) complexes with biologically produced ferric ligands strong enough to prevent Fe(III) precipitation (typically known as siderophores) (Granger and Price, 1999; Macrellis et al., 2001) or by reduction of ferric species (including those present as insoluble Fe(III) oxyhydroxides) by biologically generated reductants (Guerinot, 1994; Volker and Wolf-Gladrow, 1999) to the much more soluble ferrous (Fe(II)) form. If oxygen is present, these Fe(II) species will be thermodynamically unstable and will be oxidised back to the Fe(III) form though typically Fe(II) oxidation kinetics are reasonably slow in the circumneutral pH range with the result that elevated steady-state concentrations of Fe(II) species may exist. The interaction of Fe(II) species with oxygen may result in formation, in addition to Fe(III) species, of reactive oxygen species (ROS) superoxide, hydrogen peroxide and hydroxyl radicals according to the following set of reactions (Reactions 1–3, 6 and 8 in Table 1) (Pham and Waite, 2008a), among which reaction 1 represents the oxygenation of Fe(II) with concomitant production of the superoxide radical anion, reaction 2 represents the Fe(II)-catalysed disproportionation of superoxide to hydrogen peroxide, reaction 3 represents the peroxidation of Fe(II) (the so-called Fenton reaction resulting in production of the strongly oxidising hydroxyl radical), reaction 6 represents the acid-catalysed disproportionation of superoxide and reaction 8 represents the back-reduction of Fe(III) by superoxide. While it is recognised that bacteria may themselves induce the production of reactive oxygen species in the extracellular medium (Gonzalez-Flecha and Demple, 1995; Korshunov and Imlay, 2006), there is little insight available with regard to the extent of ROS production by the above reactions in MBR or of the implications of the presence of ROS to the transformation of redox-active elements such as iron in bioreactor systems.

The above iron transformations may be mediated by the expected extensive release of soluble microbial products (SMPs) into the medium (Rittmann and McCarty, 2001) and may also be influenced significantly by changes in dissolved oxygen concentration. For example, activated sludge systems containing a pre-denitrification process, in which there is an anoxic unit prior to aeration, might be expected to exhibit dynamic transformations in iron speciation as a result of the changing oxidation–reduction potential of the medium. Additionally, iron is often added either as ferrous iron to waste streams for odour control purposes (Waltrip and Snyder, 1985) or as ferric iron to the reactor as an aid to phosphorus removal (Stumm and Morgan, 1996) with these iron additions potentially inducing additional redox transformations of iron and oxygen species within the bioreactor.

In this study, we investigate the iron species distribution and extent of transformation between iron species and the associated impact on generation of the relatively stable reactive oxygen species hydrogen peroxide in three MBRs which differ in feed iron concentration and the presence or absence of the anoxic chamber. We also examine the ferrous iron oxidation rate in the MBR in separate batch tests using MBR effluent or sludge supernatant with conclusions drawn with regard to both the bioavailability of iron in the MBR, and the possible iron uptake pathways used by the microorganisms present.

It is expected that the results of these studies will provide insight into the factors controlling iron bioavailability which, as mentioned above, would be expected to influence both the bacterial population present and the behaviour of this population, particularly with regard to release of soluble microbial products to solution which, in turn, is recognised to be largely responsible for the onset of severe membrane fouling. An understanding of iron speciation and iron transformations in the membrane bioreactor will also be critical to understanding the fate of any iron salts added as coagulants since the nature of the species formed and any transformation of these species over the time they reside in the bioreactor would be expected to influence both the phosphorus removal capability of the added coagulant as well as the implications to improvement or worsening of membrane fouling. A pre-requisite to improving phosphorus removal and/or reducing the extent of membrane fouling through coagulant addition is a sound understanding of the nature and extent of chemical (and possibly biological) transformations induced by addition of the coagulant. The relationship between iron speciation and iron species transformation and aspects of MBR performance including nutrient removal and extent of membrane fouling is of particular interest (and importance!) and will be the subject of later investigations but is outside the scope of the current study. It should also be noted that the insights into iron species and iron species transformations gained in the present study have implications to bioreactors in general though we have confined our investigations here to iron speciation and transformation kinetics in bench-scale membrane bioreactors given our planned future studies of the implications of the behaviour of this essential nutrient and coagulant element to MBR performance.

Table 1 – Model reactions involved with iron and their oxidants or reductants. References: (1) Rose and Waite, 2002; (2) Bielski et al., 1985.

No.	Reaction	Rate constant
1	$Fe(II) + O_2 \rightarrow Fe(III) + O_2^{\bullet-}$	$78\ M^{-1}\ s^{-1}$
2	$Fe(II) + O_2^{\bullet-} + 2H^+ \rightarrow Fe(III) + H_2O_2$	$1.0 \times 10^7\ M^{-1}\ s^{-1}$ (1)
3	$Fe(II) + H_2O_2 \rightarrow Fe(III) + OH^{\bullet} + OH^-$	$3.1 \times 10^4\ M^{-1}\ s^{-1}$ (1)
4	$O_2^{\bullet-} + H^+ \rightarrow HO_2^{\bullet}$	$5.0 \times 10^{10}\ M^{-1}\ s^{-1}$ (2)
5	$HO_2^{\bullet} \rightarrow O_2^{\bullet-} + H^+$	$7.9 \times 10^5\ s^{-1}$ (2)
6	$O_2^{\bullet-} + HO_2^{\bullet} + H^+ \rightarrow H_2O_2 + O_2$	$9.7 \times 10^7\ M^{-1}\ s^{-1}$ (2)
7	$SMP + OH^{\bullet} \rightarrow SMP' + O_2^{\bullet-}$	$6.6\ (g/L)^{-1}\ s^{-1}$
8	$Fe(III) + O_2^{\bullet-} \rightarrow Fe(II) + O_2$	$1 \times 10^6\ M^{-1}\ s^{-1}$

2. Materials and methods

2.1. *Membrane bioreactors*

Three lab-scale membrane bioreactors (MBRs) that slightly differ in operational or configurational parameters were