

Quantifying the Impact of Oxygen, Nitrate and Ferric Iron on Sulfate Reducing Bioreactor Design

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Abstract The efficiency of anaerobic bioreactors targeting sulfate reducing conditions is negatively impacted by the presence oxygen, nitrate and ferric iron (electron acceptors) in the influent water. The impact of the competing electron acceptors can be accounted for using by using redox stoichiometries derived from bacterial energetics. The effect of competing electron acceptors can be expressed as a function of the influent concentration, flow and reactor volume. The impact of oxygen can be mitigated by increasing the reactor volume. Nitrate has the highest potential for complete inhibition of sulfate reduction. The stoichiometric approach presented demonstrates the importance of explicitly including competing electron acceptors on the sizing of sulfate reducing bioreactors.

Key words metal removal, passive treatment, denitrification, iron reduction

Introduction

Sulfate reducing bioreactors have the potential to provide treatment of mining influenced water (MIW) with low operation and maintenance requirements. However, sulfate reducing bacteria are out competed by aerobic, denitrifying and iron reducing bacteria in the presence of oxygen, nitrate ferric iron in MIW. Empirical concentration thresholds have been proposed (e.g., Bratcova et al. 2002) but the expected impact does not always hold true in operating systems. Johnson and Hallberg (2005) attributed poor performance of sulfate reducing bioreactor in part to the high oxygen saturation of the influent MIW. However, Willow and Cohen (2003) did not see any decrease in performance for sulfate reducing bioreactors with influent oxygen concentration. The method presented in this paper will demonstrate that the extent of sulfate reducing activity is impacted by the coupled effect of the competing electron acceptor concentration and the reactor volume to flow ratio.

Methods

Thermodynamic fundamentals of bacterial energetics and growth (Rittmann and McCarty 2001) were used to develop stoichiometric relationships which are subsequently used to calculate the impact of competing electron acceptors (e.g., oxygen and) on the required volume of organic substrate. I use the derived stoichiometries to show how to relate the concentrations of oxygen and nitrate along with reactor volume to flow ratio (V/Q) to a decrease in the design volumetric sulfate reduction rate (sulfide production rate).

Glossary

V Reactor volume, m³

CCR Carbohydrate Consumption Rate, mol CH₂O/d

V/Q Reactor volume to flow ration (Empty bed contact time), d

VSPR Volumetric sulphide production rate, mol S/m³/d

VCCR Volumetric carbohydrate consumption rate, mol CH₂O/m³/d

SRR Sulfate reduction rate, mol S/m³/d

Results and Discussion

Loading rate

Metal loading rate is a key design parameter. The goal is for the metal loading to be equal to or less than the rate of reagent production. Reagent production rate must be equal to or greater than the metal loading (of potential metal precipitates). This is based on the assumption that only a stoichiometric amount of reagent will be required to achieve the desired extent of precipitation. The required units of metal loading are mol per time. Influent metal concentration of the targeted metals must be converted from grams (g) to mol. Typical target metals for sulfide precipitation with the molecular weight conversion factor are presented in the Table below.

Metal, mol/L = Cd/MW_{Cd} + Cu/MW_{Cu} + Fe/MW_{Fe} + Ni/MW_{Ni} + Pb/MW_{Pb} + Zn/MW_{Zn}
 where metal concentration is in g/L and MW_{Me} is the molecular weight of the respective metal (e.g., Cd).

Once the metal concentration in mol per liter (Me) is determined. The volume of the bioreactor based on the metal loading criteria can be estimated if the flow rate (Q) is known. To determine the reactor volume, we must balance the volumetric rate of reagent production with the target metal loading.

Metal sulfide precipitation

For the initial examination of how this applies to metals, we will look at the case of metal sulfide precipitation. For any volumetric sulfide production rate (VSPR), the reactor volume would be:

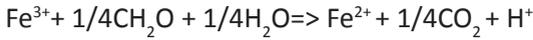
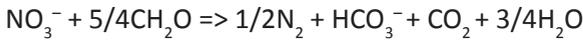
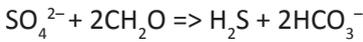
$$V_{Me}, m^3 = \frac{Q Me}{VSPR}$$

A typical VSPR value used for design is 0.3 mol S/m³/d (Willow and Cohen 2003). However, VSPR rates will vary with influent water composition, specific bioreactor substrate mix, temperature and age. Competing electron acceptors are currently not included in the analysis and can reduce the volumetric sulfide production rate.

Competing electron acceptors of concern are oxygen, nitrate and iron. Oxygen and iron are commonly measured in MIW yet not included in the current analysis protocol. One way to approach the impact of competing electron acceptors is to increase the required volume of the substrate to account for the other electron acceptors.

$$V_{design}, m^3 = V_{Me} + V_{O_2} + V_{Fe^{3+}} + V_{NO_3^-}$$

Stoichiometries for the potentially competing electron acceptors oxygen, nitrate and ferric iron are shown below with the sulfate stoichiometry for reference.



The sulfide production rate is associated with a carbohydrate (CH_2O) consumption rate. The impact of the consumption of available carbohydrate by the other electron acceptor can be estimated using the relationships shown in the table below.

Table 1 Mol of carbohydrate consumption per mole of electron acceptor

Electron acceptor	Mol	Mol CH_2O required per mole acceptor
SO_4^{2-}	1	2.2
O_2	1	2.5
NO_3^-	1	2.5
Fe^{3+}	1	0.5

The potential impact of any of the three more energetically favorable electron acceptors can be estimated using the above stoichiometries. These stoichiometries include cell synthesis. Cell synthesis demands will increase the effect of the competing electron acceptors.

Example:

An example MIW is used to demonstrate the analysis method (shown in Table 1) for treatment in a sulfate reducing bioreactor. For this example, pH considerations are not included. The design flow is 30,000 L/d.

Table 2 Major water constituents for example system analysis

Constituent	Conc., mg/L
Zn^{2+}	6.5
SO_4^{2-}	960
O_2	8
Fe^{3+}	55
NO_3^-	50

The approach is to calculate the volume required for metals and competing electron acceptor. The method to calculate the volume for metal removal was shown above. The volume for the competing electron acceptors can be calculated if we relate the design sulfide production rate to a carbohydrate consumption rate. For a value of 0.3 mol S/m³/d the equivalent carbohydrate consumption rate (CCR), based on our stoichiometry, is 0.66 mol of CH₂O/m³/d. We can then use the stoichiometries presented in Table 1 to determine the additional volume for each of the competing electron acceptors. For this example, we are using the 0.3 mol S/m³/d as the design point. The values will be different for another volumetric sulfide production rate. The analysis presented below is developed on this basis and only includes the analysis for the impact of oxygen.

Influent metals for MeS

Constituent	Conc., mg/L	MW	Conc., mM/L	Loading, M/d
Zn ²⁺	6.5	65	0.1	3

Calculations

Influent sulfate load

Constituent	Conc., mg/L	MW	Conc., mM/L	Loading, M/d
SO ₄ ²⁻	960	96	10	300

Calculations

Required sulfate reduction

Constituent	Metal load, M/d	Sulfate needed, M/d	M CH ₂ O required/d (CCR)
SO ₄ ²⁻	3	3*	6.6

Calculations

* important to check that sulfate needed < sulfate influent

Influent competing electron acceptors

Constituent	Conc., mg/L	MW	Conc., mM/L	Loading, M/d	M CH ₂ O required/d
O ₂	8	32	0.25	7.5	18.75

Calculations

$$V_{Me}, m^3 = \frac{CCR_{Me}}{VCCR} = \frac{6.6 \text{ moles } CH_2O/d}{0.6 \text{ moles } CH_2O/m^3/d} = 11 m^3$$

$$V_{O_2}, m^3 = \frac{CCR_{O_2}}{VCCR} = \frac{18.75 \text{ moles } CH_2O/d}{0.6 \text{ moles } CH_2O/m^3/d} = 31.25 m^3$$

Total volume required is 42.25 m³/d.

This example illustrates an important point on sizing of sulfate reducing bioreactors. The reactor size based on metal removal only would have resulted in a volume of 11 m³ relative to the size needed to accommodate the oxygen impact. Thus, the reactor volume would have been undersized by a factor of 4. The above analysis was completed for a range of electron acceptor concentrations and reactor volume to flow ratios.

Competing electron acceptors impacts can be presented in units of equivalent mol of sulfate reduction/ m^3/d . This allows for a visual comparison of the potential reduction in sulfate reduction rate as a function of competing electron acceptors concentration, reactor volume and flow. Figures 1, 2 and 3 present the results for three different concentrations of the three competing electron accepts for reactor volume to flow ratios of 1 to 20 days.

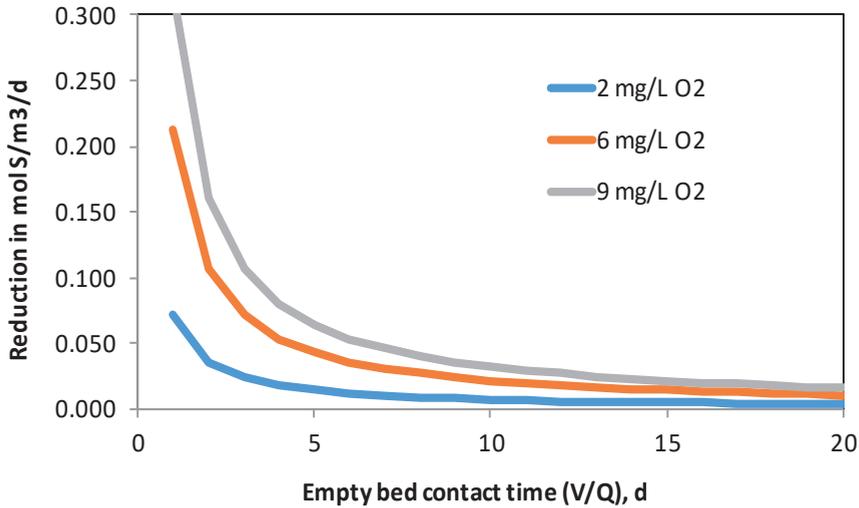


Figure 1 Calculated reduction in volumetric sulphate reduction rate (SRR) by oxygen (O₂) as a function of the reactor volume to flow ratio (V/Q).

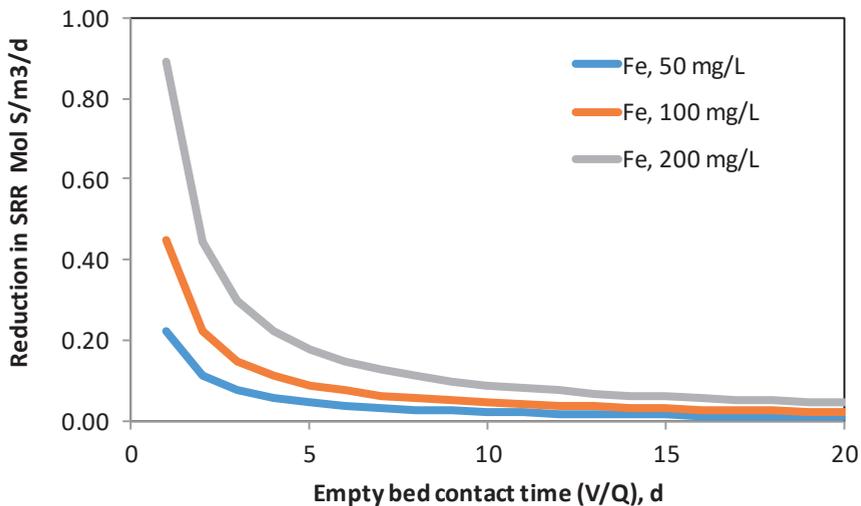


Figure 2 Calculated reduction in volumetric sulphate reduction rate (SRR) by ferric iron (Fe) as a function of the reactor volume to flow ratio (V/Q).

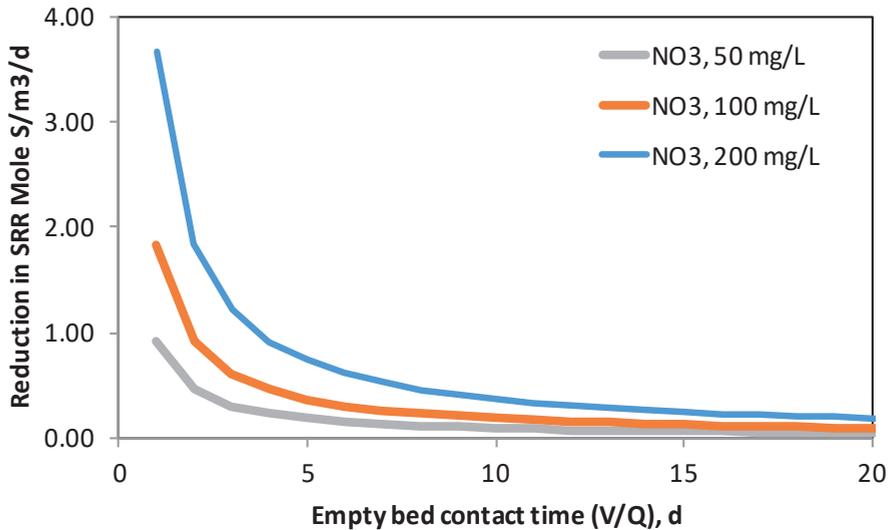


Figure 3 Calculated reduction in volumetric sulphate reduction rate (SRR) by nitrate (NO_3) as a function of the reactor volume to flow ratio (V/Q).

Implications of the dissolved oxygen concentration and EBCT on inhibition of sulfate reduction rate (SRR):

- Low DO (2 mg/L) coupled with low V/Q (1 to 5 days) will reduce effective SRR by 5 to 50%
- High DO (9 mg/L) coupled with low V/Q (1 to 5 days) will reduce effective SRR by 20 to 100%.
- Low DO (2 mg/L) with high V/Q (> 15d) will have a very low impact on effective SRR (reduction \leq 2 to 3%)
- High DO (9 mg/L) with high V/Q (> 15d) will have a low impact on effective SRR (reduction \leq 7 to 14%)

Implications of the ferric iron concentration and V/Q on inhibition of sulfate reduction rate (SRR):

- Moderate Fe (50 mg/L) coupled with low V/Q (1 to 5 days) can reduce effective SRR by 15 to 100 %
- High Fe (200 mg/L) coupled with low V/Q (1 to 5 days) can reduce effective SRR by \leq 60 to 100 %.
- Moderate Fe (50 mg/L) with high V/Q (> 15d) will have a low impact on effective SRR, reduction \leq 5 to 10 %)
- High Fe (200 mg/L) with high V/Q (> 15d) will have a moderate impact on effective SRR, reduction \leq 20 to 40 %)

Implications of the nitrate concentration and EBCT on inhibition of sulfate reduction rate (SRR):

- Moderate NO_3 (50 mg/L) coupled with low V/Q (1 to 5 days) can reduce effective SRR by 60 to 100 %
- Moderate NO_3 (50 mg/L) with high V/Q (> 15d) will have a low impact on effective SRR, reduction ≤ 20 %
- High NO_3 (200 mg/L) with high V/Q (> 15d) will have a high impact on effective SRR (reduction of 80 to 100 %)

Conclusions

The analysis supports that it is possible to achieve good sulfate reducing activity in the presence of oxygen saturated MIW if the volume is increased proportionately. If only metal loading coupled with sulfide production had been considered for a model MIW, the reactor volume would be undersized by a factor of 4 for a volume to flow ratio of 2 d. This is equivalent to an apparent volumetric sulfate reduction rate of 0.075 mol/m³/d compared to the typical proposed value of 0.3 mol/m³/d. The analysis tool developed herein illustrates the importance of explicitly including competing electron acceptors on the sizing of sulfate reducing bioreactors.

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