Supporting Information

for

Understanding the Composition and Spatial Distribution of Biological Selenate Reduction

Products for Potential Selenium Recovery
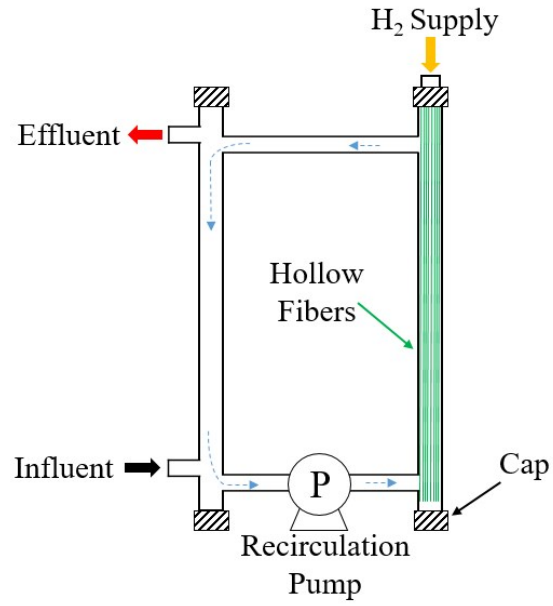
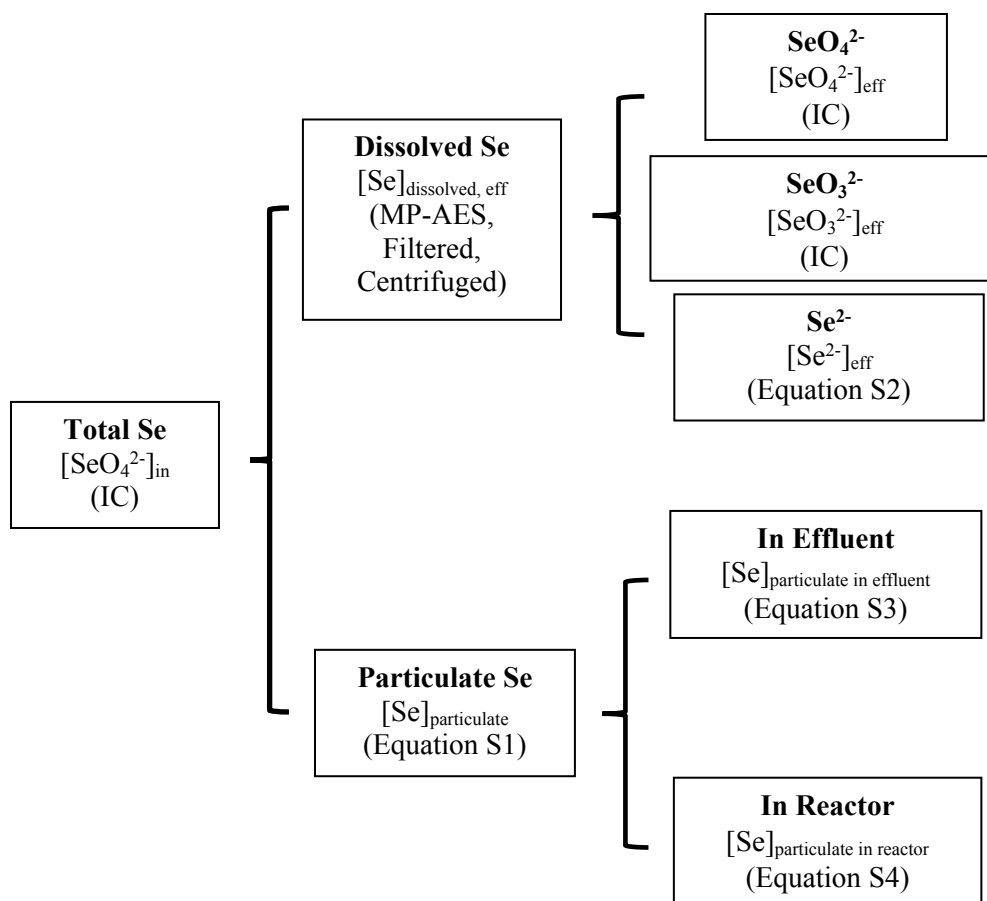Figure S1. A schematic image of the H_2-based membrane biofilm reactor (MBfR)

Figure S2. Methods for selenium speciation

Notes:

1) Equation S1: $[Se]_{particulate} = [SeO_4^{2-}]_{in} - [Se]_{dissolved,\ eff}$

   Equation S2: $[Se^{2-}]_{eff} = [Se]_{dissolved,\ eff} - [SeO_4^{2-}]_{eff} - [SeO_3^{2-}]_{eff}$

   Equation S3: $[Se]_{particulate\ in\ effluent}$ = total selenium in the effluent sample (measured by Microwave Plasma-Atomic Emission Spectrometer, model 4100 MP-AES, Agilent Technologies, USA) - total selenium in the effluent sample after the sample was centrifuged at 21,000 rcf for 30 min and then filtered by a 20 nm-pore size syringe filter.

   Equation S4: $[Se]_{particulate\ in\ reactor} = [Se]_{particulate} - [Se]_{particulate\ in\ effluent}$

2) IC: Ion Chromatography; MP-AES: Microwave Plasma-Atomic Emission Spectrometer.

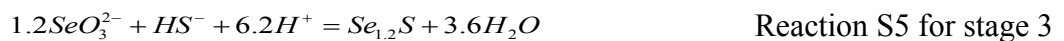**Table S1. Operating conditions for the three stages**

Stage	Flow rate (mL/day)	HRT (day)	Influent SeO_4^{2-} concentration (mg Se/L)	SeO_4^{2-} loading rate (mg Se/m²-day)	Influent SO_4^{2-} concentration (mg S/L)	SO_4^{2-} loading rate (g S/m²-day)
1	107	0.28	4.2	285	1,500	102
2	214	0.14	4.2	570	1,500	204
3	428	0.07	4.2	1,140	1,500	407

H₂ supply and consumption analysis for the three stages:

The theoretical maximum H_2 supply rate was approximately 220 mg H_2/m²-day based on Tang, et al. (2012),[1] considering that polypropylene fibers were used in this study and the H_2 pressure was 5 psig.

Accurate calculation of the H_2 consumption requires the knowledge on the percentages of selenate reduced to Se^0 and selenium sulfides, respectively. This knowledge was available in stage 1 since all selenate was reduced to Se^0. However, this information could not be determined in stages 2 and 3. Therefore, two extreme scenarios were used to estimate the H_2 consumption range in stages 2 and 3. In the first scenario, Se^0 was assumed to be the only particulate selenium product, and the corresponding reactions were S1, S2, and S3. In the second scenario, selenium sulfide was assumed to be the only particulate selenium product, and the corresponding reactions were S2, S3, and S4 for stage 2 (or S5 for stage 3). Equations S1-S3 were based on the stoichiometric method in Rittmann and McCarty (2012),[2] Equation S4 was based on the typical Se:S ratio in 60 EDX spectra of the selenium sulfides in the stage 2 effluent, and Equation S5 was based on the typical Se:S ratio in 35 EDX spectra of the selenium sulfides in the stage 3 effluent.

$$0.5H_2 + 0.129SeO_4^{2-} + 0.045CO_2 + 0.011HCO_3^- + 0.011NH_4^+ + 0.258H^+$$
$$= 0.617H_2O + 0.011C_5H_7O_2N + 0.129Se^0$$
Reaction S1

$$0.5H_2 + 0.182SeO_4^{2-} + 0.127CO_2 + 0.032HCO_3^- + 0.032NH_4^+$$
$$= 0.468H_2O + 0.032C_5H_7O_2N + 0.182SeO_3^{2-}$$
Reaction S2

$$0.5H_2 + 0.089SO_4^{2-} + 0.057CO_2 + 0.014HCO_3^- + 0.014NH_4^+ + 0.134H^+$$
$$= 0.045H_2S + 0.045HS^- + 0.486H_2O + 0.014C_5H_7O_2N$$
Reaction S3

$$1.7SeO_3^{2-} + HS^- + 9.2H^+ = Se_{1.7}S + 5.1H_2O$$
Reaction S4 for stage 2

$$1.2SeO_3^{2-} + HS^- + 6.2H^+ = Se_{1.2}S + 3.6H_2O$$
Reaction S5 for stage 3
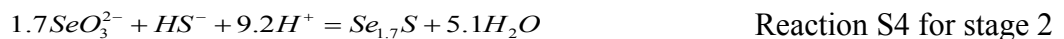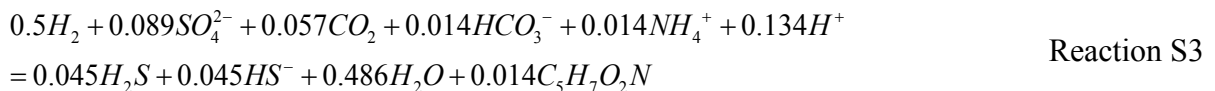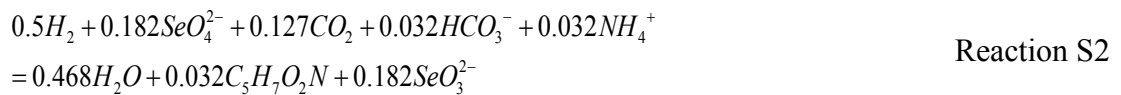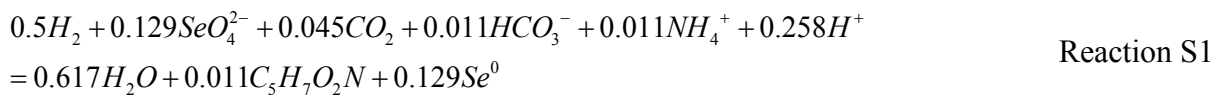
The estimated H_2 consumption for the three stages are summarized in Table S2. The estimated H_2 consumption for stage 1 was approximate 33 mg H_2/m^2-day (Table S2). The estimated H_2 consumption for stage 2 might range from 57 to 127 mg H_2/m^2-day, and the range of H_2 consumption for stage 3 might range from 105 to 219 mg H_2/m^2-day.

Table S2. Estimated H_2 consumption at the three stages when they reached steady state

Stage	Scenario	Reactions	SeO_4^{2-} or SO_4^{2-} reduction (mg Se or S/L)	H_2 consumption flux by reactions (mg H_2/m^2-day)	Total H_2 consumption flux (mg H_2/m^2-day)
1	1	S1	4.1 mg Se/L[2]	27[6]	33
		S2	0 mg Se/L[2]	0[7]	
		S3	0.25 mg S/L[3]	6.0[8]	
2	1[1]	S1	4.0 mg Se/L[2]	53	57
		S2	0.1 mg Se/L[2]	2	
		S3	0.05 mg S/L[3]	2	
	2[1]	S2	4.0 mg Se/L[2]	79	127
		S3	1.0 mg S/L[4]	48	
		S4	Did not consume H_2		
3	1[1]	S1	2.7 mg Se/L[2]	72	105
		S2	1.5 mg Se/L[2]	28	
		S3	0.05 mg S/L[3]	5	
	2[1]	S2	4.2[2]	79	219
		S3	1.5[5]	140	
		S5	Did not consume H_2		

Notes:
1. In Scenario 1 Se^0 was assumed to be the only particulate selenium product, and in Scenario 2, selenium sulfides ($Se_{1.7}S$ for stage 2, and $Se_{1.2}S$ for stage 3) was assumed to be the only particulate selenium product.
2. Values were obtained from Figure 1.
3. Values were obtained from Table 1.
4. The values were based on the following stoichiometry: 1) 4.0 mg $Se_{1.7}S$-Se/L produced in Reaction S4 → 0.95 mg SO_4^{2-}-S/L reduction in Reaction S3, 2) 0.05 mg SO_4^{2-}-S/L reduction in Reaction S3 as dissolved sulfide in effluent.

5. The values were based on the following stoichiometry: 1) 4.2 mg $Se_{1.2}S$-Se/L produced in Reaction S5 → 1.42 mg SO_4^{2-}-S/L reduction in Reaction S3, 2) 0.05 mg SO_4^{2-}-S/L reduction in Reaction S3 as dissolved sulfide in effluent.

6. For Reaction S1, the required H_2 was $\dfrac{(0.5\times2)\text{g } H_2\times4.1\text{mg Se/L}}{0.129\times79\text{g Se}}=0.4\text{mg } H_2/\text{L}$. The Required H_2 flux was

$\dfrac{0.4\text{mg } H_2/\text{L}\times Q}{A} = 27\text{mg } H_2/\text{m}^2\text{-day}$, where Q is the flow rate (*i.e.*, 107 mL/day) and A is the membrane

surface area (*i.e.*, 1.57×10^{-3} m^2).

7. For Reaction S2, the required H_2 was $\dfrac{(0.5\times2)\text{g } H_2\times0\text{mg Se/L}}{0.182\times79\text{g Se}}=0\text{mg } H_2/\text{L}$. The Required H_2 flux was

$\dfrac{0\text{mg } H_2/\text{L}\times Q}{A} = 0\text{mg } H_2/\text{m}^2\text{-day}$.

8. For Reaction S3, the required H_2 was $\dfrac{(0.5\times2)\text{g } H_2\times0.25\text{mg S/L}}{0.089\times32\text{g S}}=0.088\text{mg } H_2/\text{L}$. The Required H_2 flux

was $\dfrac{0.088\text{mg } H_2/\text{L}\times Q}{A} = 6\text{mg } H_2/\text{m}^2\text{-day}$.

References

1. B.E. Rittmann and P.L. McCarty. Environmental biotechnology: principles and applications. Tata McGraw-Hill Education. 2012.

2. Y. Tang, C. Zhou, S.W. Van Ginkel, A. Ontiveros-Valencia, J. Shin and B.E. Rittmann. Hydrogen permeability of the hollow fibers used in H_2-based membrane biofilm reactors. *J. Membr. Sci.* 2012, 407-408, 176-183. doi: 10.1016/j.memsci.2012.03.040