The Effect of Sulfidation on Solubility of Silver Nanoparticles On Water Treatment Membranes

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Introduction

Biofouling hinders water treatment membranes. Coating them with silver nanoparticles (AgNPs) increases their antimicrobial biofouling resistance. Unfortunately, AgNPs are soluble, limiting their long-term effectiveness. AgNPs react with Sodium Sulfide (Na_2S) to form silver sulfide (Ag_2S). This partially sulfidizes the AgNPs changing both the solubility and antimicrobial properties.

Objective and Hypothesis

Objective: Characterize the change in AgNPs solubility due to partial sulfidation in order to correlate with changes in antimicrobial activity and biofouling resistance.

Hypothesis: There is a threshold of sulfidation, when a lower solubility of AgNPs retains enough antimicrobial properties for biofouling control.

Experimental Design

Membranes were prepared with AgNPs then reacted with different concentrations of Na_2S (10^{-5}M, 10^{-3}M, and 10^{-1}M). Cutouts were agitated in 18.2MΩ deionized water up to 6 hours. The water was analyzed for silver dissolved from the cutouts then the cutouts were digested in 10% trace metal nitric acid, to find the mass of silver remaining on the membrane. Analysis used ICP-MS. All experiments were repeated 3 times.

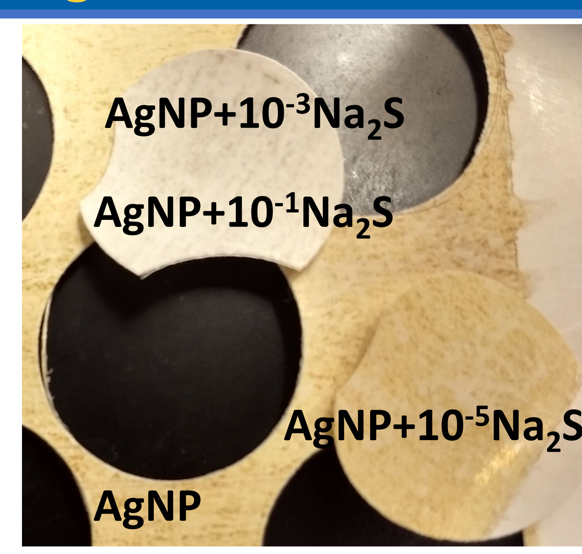

Figure 1: *Appearance of Membranes*

Two Data Sets

The experiment produced 2 data sets: the mass of AgNPs remaining on the membrane and the mass of AgNPs dissolved from the membrane. The two data sets were complimentary; the mass in solution should equal the mass dissolved from the membrane and the sum should equal the original AgNP loading of the cutout.

Combining the data sets, the average mass of AgNPs was 2618ng with a standard deviation of 397ng. This closely matches the mean (2471ng) and standard deviation (468ng)across a previously tested AgNP membrane.

The AgNP+$10^{-5}Na_2S$ cutouts had the highest standard deviation (509ng) of the tested membranes. There may have been large variations on that membrane's original AgNP loading.

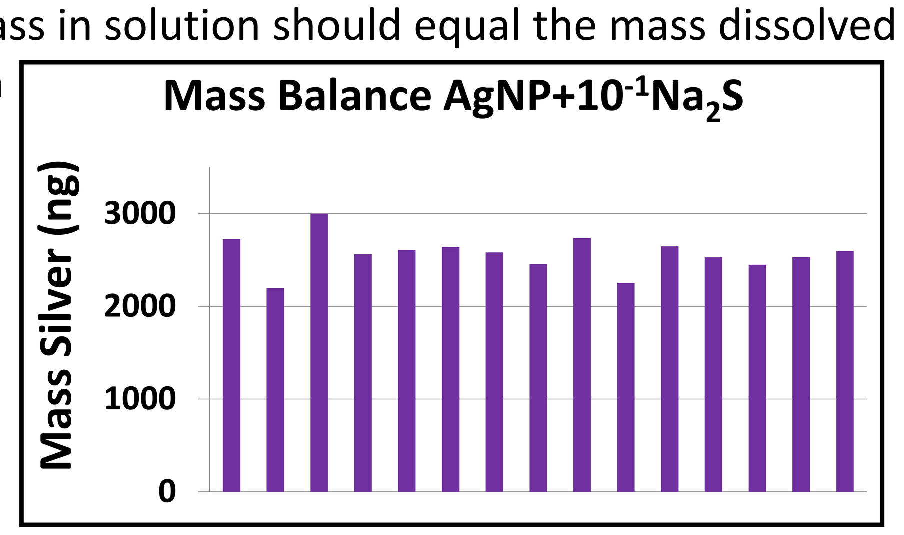

Figure 2: *The mass balance of high sulfidized AgNPs, showing good data consistency among cutouts.*

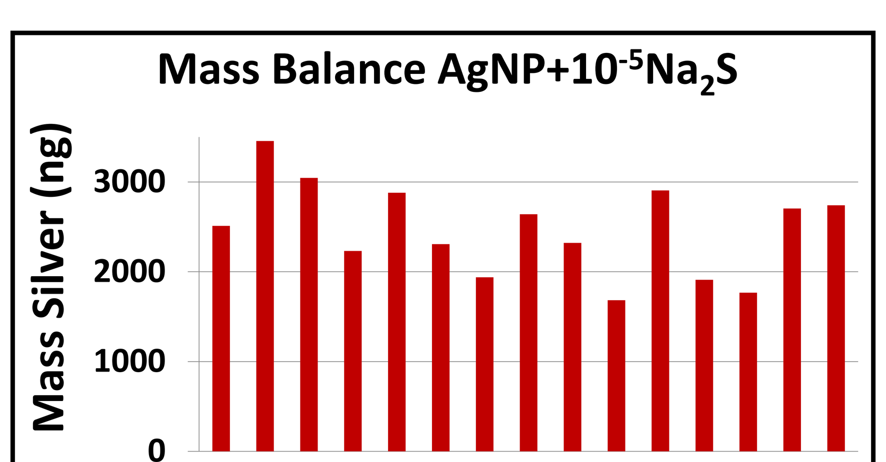

Figure 3: *The mass balance of low sulfidized AgNPs, showing poor data consistency among cutouts.*

More Sulfidation Means Less Solubility

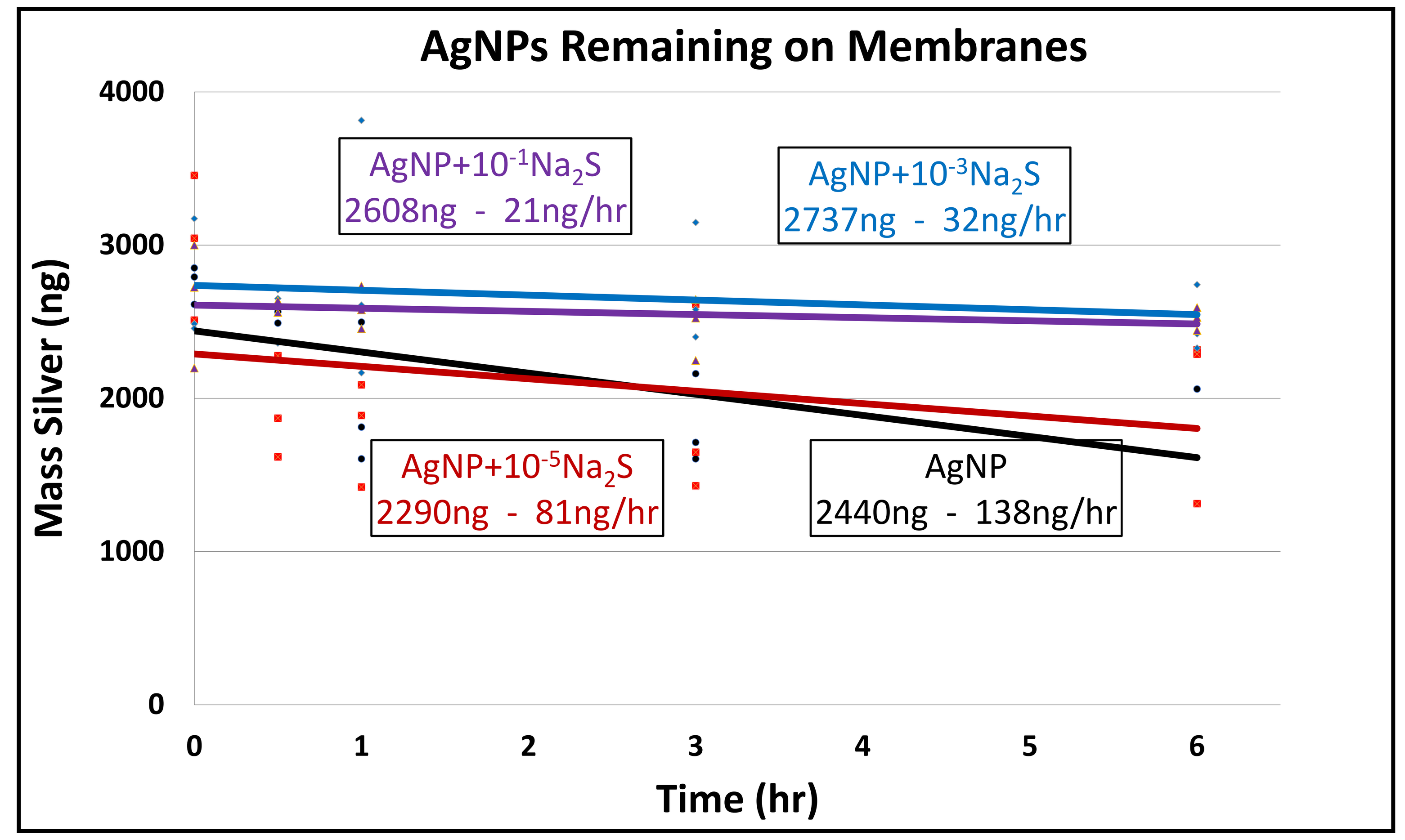

Figure 4: *Graph of the first data set – mass of AgNPs remaining on the membrane. The slope is the average rate of dissolution.*

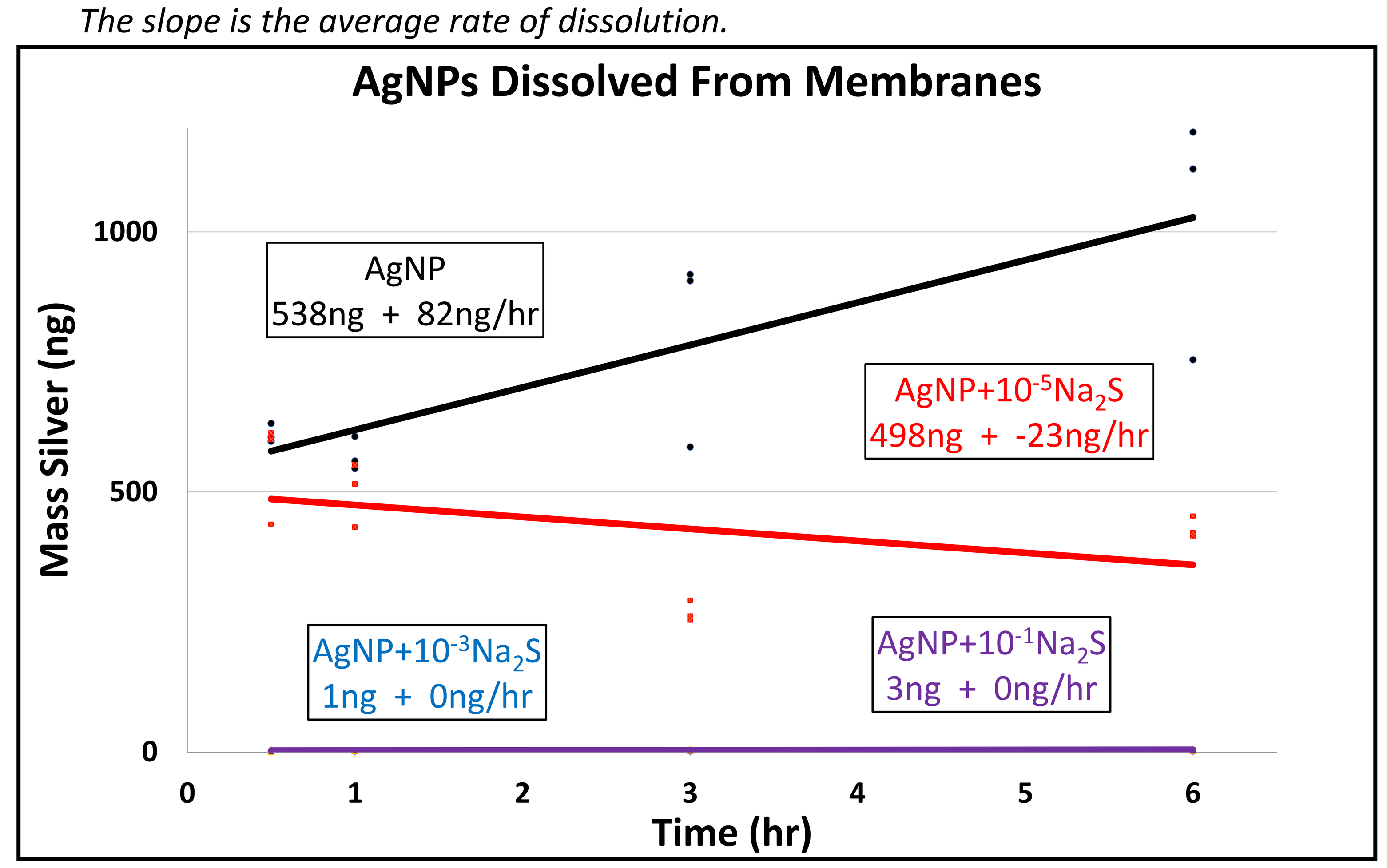

Figure 5: *Graph of the second data set – mass of AgNPs dissolved from the membrane. The slope is the average rate of dissolution.*

Initial and Sustained Solubility

Table 1: *The rate of AgNPs dissolving during the initial 30 minutes, compared to the next sustained 330 minutes. Units are ng per minute per cm² of membrane.*

	AgNP	AgNP+$10^{-5}Na_2S$	AgNP+$10^{-3}Na_2S$	AgNP+$10^{-1}Na_2S$
Initial loss from membrane	10.4	36.0	4.4	1.3
Initial loss to solution	20.4	18.4	0.0	0.1
Sustained loss from membrane	1.2	-0.3*	0.6	0.3
Sustained loss to solution	1.4	-0.4*	0.0	0.0

*It is unlikely that the AgNP+$10^{-5}Na_2S$ membrane was gaining AgNPs. This membrane had the highest standard deviation. (see figures 3 and 5)

Initial and Sustained Solubility

During the first 30 minutes there was significant dissolution of AgNPs from membranes with zero or low (10^{-5}M) sulfidation. Membranes with more sulfidation (10^{-3}M and 10^{-1}M) had a 93% decrease in the initial rate of AgNPs dissolving.

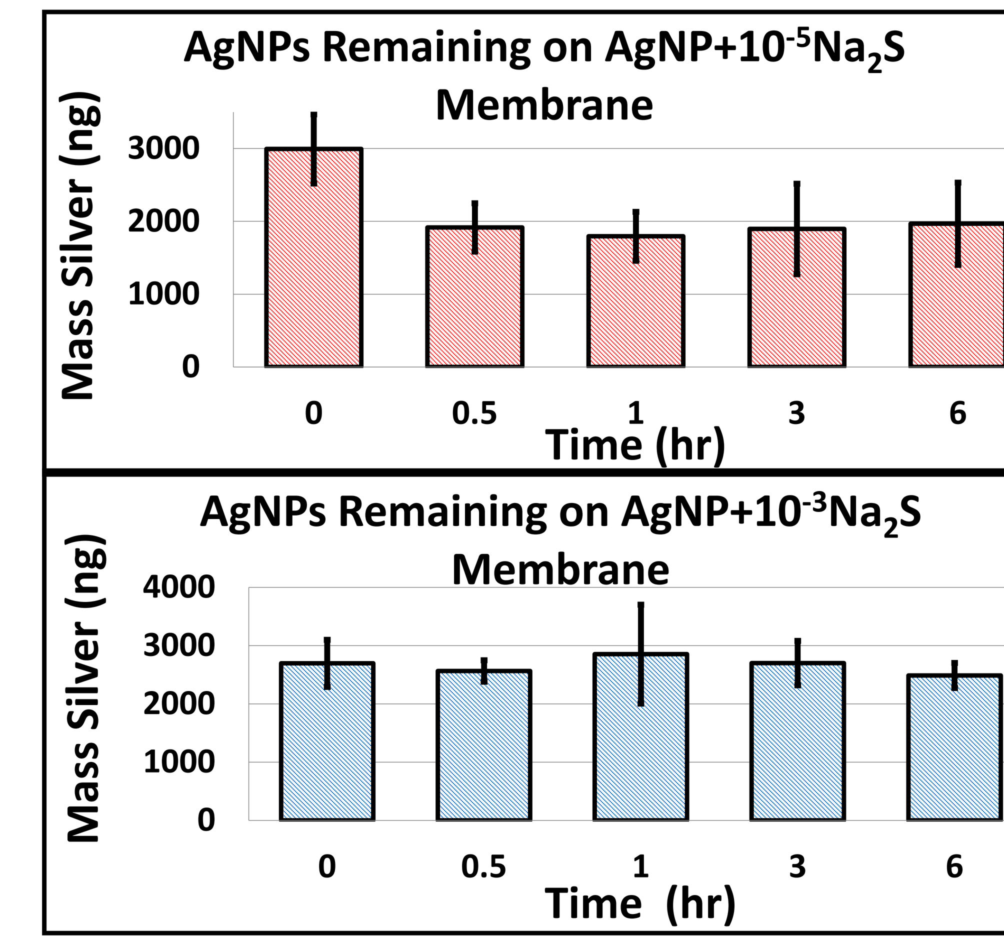

Figure 6: *Comparison of Initial Rate of AgNPs dissolving from the membranes..*

During the next 330 minutes there was significant dissolution of AgNPs from membranes with zero sulfidation. Membranes with more sulfidation (10^{-5}M, 10^{-3}M, and 10^{-1}M) had an 83% decrease in the sustained rate of AgNPs dissolving.

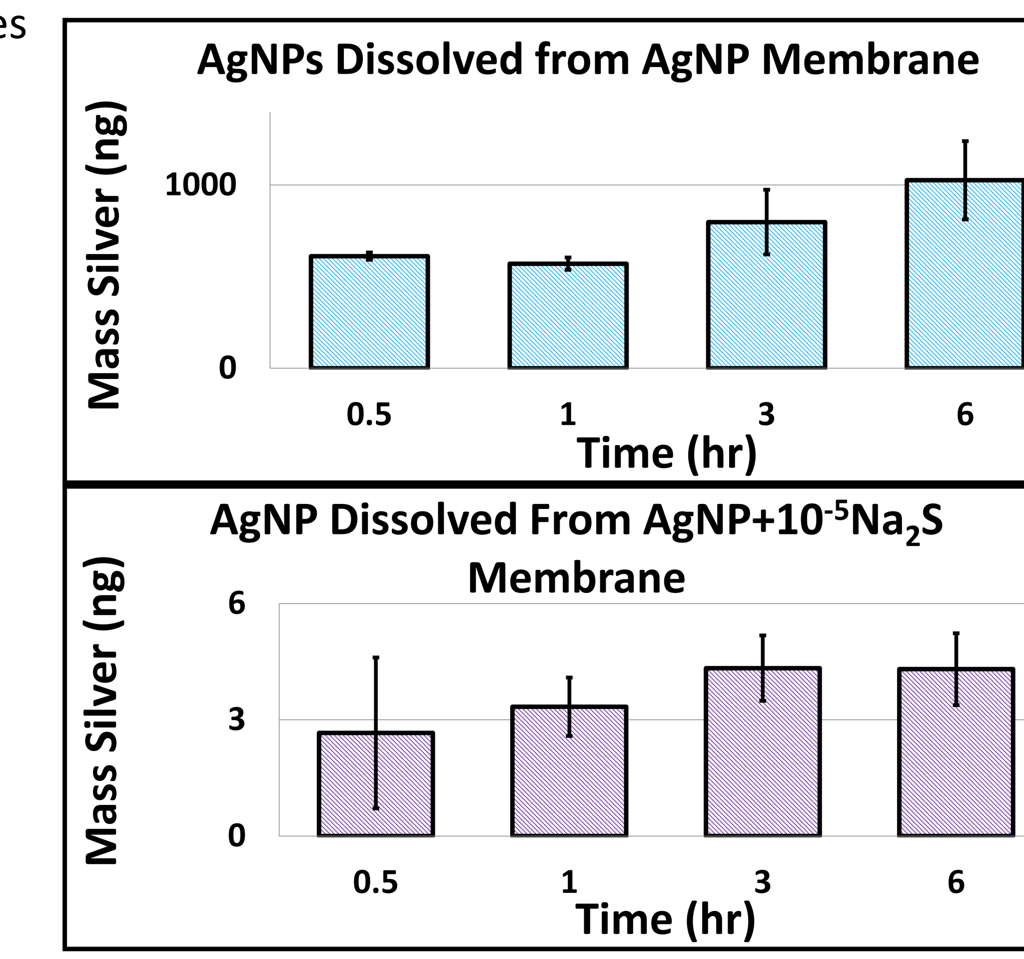

Figure 7: *Comparison of sustained Rate of AgNPs dissolving from the membranes. Note the vertical scale change.*

What to Try Next

Analyze more membranes with sulfidation between 0 and 10^{-3}M Na_2S.
Increase the time to see longer term dissolution rates.
Characterize the surface of the membranes with SEM.
Correlate this data with antimicrobial activity.

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