Adsorption of Dissolved Metals in the Berkeley Pit using Thiol-Functionalized Self-Assembled Monolayers on Mesoporous Supports (Thiol-SAMMS) – 10150

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ABSTRACT

The Berkeley Pit in Butte, Montana, is heavily contaminated with dissolved metals. Adsorption and extraction of these metals can be accomplished through the use of a selective adsorbent. For this research, the adsorbent used was thiol-functionalized Self-Assembled Monolayers on Mesoporous Supports (thiol-SAMMS), which was developed at Pacific Northwest National Laboratory (PNNL). Thiol-SAMMS selectively binds to numerous types of dissolved metals. The objective of this research was to evaluate the loading and kinetics of aluminum, beryllium, copper, and zinc on thiol-SAMMS. For the loading tests, a series of Berkeley Pit water to thiol-SAMMS ratios (mL:g) were tested. These ratios were 1000:1, 500:1, 100:1, and 50:1. Berkeley Pit water is acidic (pH ≈ 2.5). This can affect the performance of SAMMS materials. Therefore, the effect of pH was evaluated by conducting parallel series of loading tests wherein the Berkeley Pit water was neutralized before or after addition of thiol-SAMMS, and a series of kinetics tests wherein the Berkeley Pit water was either not neutralized or was neutralized before addition of thiol-SAMMS. For the kinetics tests, one Berkeley Pit water to thiol-SAMMS ratio was tested, which was 2000:1. The results of the loading and kinetics tests suggest that a significant decrease in dissolved metal concentration at Berkeley Pit could be realized through neutralization of Berkeley Pit water. Thiol-SAMMS technology has a limited application under the highly acidic conditions posed by the Berkeley Pit. However, thiol-SAMMS may possibly provide a secondary remedial technique to remove dissolved metals to concentrations below drinking water standards. More research is necessary to optimize a remedial strategy, including SAMMS technology, for remediation of Berkeley Pit.

INTRODUCTION

Safe and healthy water supplies are a serious global issue. Fresh water supplies can become contaminated by many different types of chemicals originating from industrial and agricultural processes. The Berkeley Pit in Butte, Montana, is a former open pit mine that today contains over 40 billion gallons of contaminated water as a result of years of surface water and groundwater runoff into the pit [1]. Many different remediation techniques exist for remediating aquatic environments. Remediation technologies are usually specific for each type of chemical, such as organics and heavy metals. In this research the adsorption of aluminum, beryllium,

copper, and zinc was tested by using thiol-functionalized Self-Assembled Monolayers on Mesoporous Supports (thiol-SAMMS), a selective adsorbent developed at Pacific Northwest National Laboratory (PNNL).

The United States Environmental Protection Agency (EPA) sets National Primary and Secondary Drinking Water Regulations (NPDWRs and NSDWRs, respectively) for different contaminants in drinking water. Primary regulations are enforceable and are set for contaminants that can pose health hazards, whereas secondary regulations are non-enforceable but recommended because of aesthetic issues in drinking water. Regulations are set in the form of maximum contaminant levels (MCLs). Beryllium and copper are both regulated by primary regulations. Beryllium has a MCL of 0.004 mg/L, and copper has a MCL of 1.3 mg/L. Aluminum and zinc are both regulated by secondary regulations. Aluminum has a MCL range of 0.05 to 0.2 mg/L, and zinc has a MCL of 5 mg/L [2].

The United States Agency for Toxic Substances and Disease Registry (ATSDR) and the EPA have information on the environmental and health effects of aluminum, beryllium, copper, and zinc, as well as many other toxic substances. Beryllium can be harmful if inhaled or ingested. It can potentially cause acute beryllium disease and, more seriously, chronic beryllium disease (CBD) can form in people sensitive to beryllium [3]. Aluminum is also potentially harmful to human health. People who are exposed to aluminum in high levels may develop Alzheimer's disease. Although some studies support this finding, there are others that do not. In addition, some people with kidney disease have a high concentration of aluminum in their bodies. Some have developed bone or brain diseases that may have been caused by an excess of aluminum [4]. In addition, copper and zinc are both necessary for life but can be harmful at high concentrations [5, 6, 7].

The Berkeley Pit operated as an open pit mine from 1955 to 1982. Groundwater inflow and surface water runoff were continually pumped out of the mine during the 27 years of operation. Once the pit closed, the pumps were shut off and water began filling the mine shafts and the pit [8]. Today, the pit holds over 40 billion gallons of water, and the water level is approximately 5,280 feet above sea level [1]. The Berkeley Pit surface water has a pH of about 2.5 through a depth of approximately 750 feet. The EPA and the Montana Department of Health and Environmental Sciences set a maximum critical water level (CWL) for the Berkeley Pit of 5,410 feet above mean sea level (ft msl), at which point the pit will have approximately 64 billion gallons of water. The CWL was set to prevent Berkeley Pit water from entering the alluvial aquifer or Silver Bow Creek drainage [9]. The 1994 EPA Record of Decision for Silver Bow Creek/Butte Area estimates that if no remedial efforts are carried out in the Berkeley Pit, the CWL will be approached by 2015 [9].

Many different methods exist for removing dissolved metals from water. Some of the more common methods are ion-exchange, membrane processes, and adsorption. Ion-exchange is a reaction between ions in a liquid phase and ions in a solid phase. In this reaction, ions from the liquid solution are exchanged with different ions from the solid solution [10]. Membranes allow exchange of ions between two solutions. Selectively permeable membranes may be made out of different materials such as zeolite [11]. Selectively permeable membranes allow only certain ions to pass between the solutions. The focus of this research is on adsorption. In adsorption, an adsorbent binds to ions in solution. An adsorbent usually has a high surface area to mass ratio to allow more binding sites on the adsorbent.

Alternatively, novel new engineered materials, such as thiol-SAMMS, present additional possible means of remediation. Thiol-SAMMS has a thiol functional group, which is a hydrogen bonded to a sulfur (HS). Metals bind to the sulfur in this group and remove the bound thiol hydrogen. Thiol-SAMMS has a high surface area to mass ratio (approximately ~800 to 1000 m^2/g). It selectively adsorbs certain metals, such as mercury, copper, and silver. It adsorbs minimal amounts of alkali and alkali earth metals such as sodium, magnesium, and calcium [12]. For certain metals, thiol-SAMMS has a large loading capacity, meaning that a relatively large amount of metal ions can adsorb onto a small amount of thiol-SAMMS. Because of these qualities, thiol-SAMMS is a good choice of adsorbent to test in Berkeley Pit water. The research presented here shows the results of adsorption tests using thiol-SAMMS adsorbent on Berkeley Pit water.

MATERIALS AND METHODS

Loading Experiments

A series of loading experiments were run to determine the mass of dissolved metals, within Berkeley Pit water, that could be adsorbed per mass of thiol-SAMMS given a 24 hour contact time. Berkeley Pit water was tested from a depth of 750 feet. The ratios of Berkeley Pit water to mass of thiol-SAMMS tested were 1000:1, 500:1, 100:1, and 50:1 (Table I). In addition, because Berkeley Pit water is acidic (pH ≈ 2.5), a parallel series of experiments were conducted wherein one set of solutions was neutralized with 5M LiOH prior and one set subsequent to the addition of thiol-SAMMS. For each sample, a duplicate, and sometimes a triplicate, was run. Six control samples of Berkeley Pit water from a depth of 750 feet were also taken: two without adding anything, three neutralized to a pH ≈ 7, and one neutralized to a pH ≈ 8. A total of twenty-five solutions were prepared for the loading experiment for Berkeley Pit water from a depth of 750 feet.

Table I: Ratios of Berkeley Pit water to thiol-SAMMS for loading experiments

Ratio	Volume of Berkeley Pit Water from 750 feet deep	Thiol-SAMMS
(mL:g)	(mL)	(g)
1000:1	125	0.125
500:1	62.5	0.125
100:1	12.5	0.125
50:1	12.5	0.250

Experiments were conducted by adding the measured volume of Berkeley Pit water to a clean Nalgene high-density polyethylene (HDPE) bottle. The density of Berkeley Pit water from a depth of 750 feet was measured to be approximately 1.006 g/mL. This is greater than the density of deionized (DI) water, which was measured to be approximately 0.991 g/mL. The measured

volume of Berkeley Pit water for each test solution (Table I) was verified by weighing the solutions using a four-place analytical mass balance. Moreover, the density of Berkeley Pit water from a depth of 750 feet was used to calculate the mass and volume of each solution.

The required mass of thiol-SAMMS for each test solution (Table I) was measured using a four-place analytical mass balance and placed in a clean Nalgene HDPE bottle. Thiol-SAMMS is hydrophobic and must be preconditioned with ethanol in order for dissolved metals in Berkeley Pit water to adsorb onto thiol-SAMMS. Ethanol was added to the thiol-SAMMS to wet all the thiol-SAMMS in the bottle.

For each solution neutralized before the addition of thiol-SAMMS, the volume of Berkeley Pit water in the first bottle was neutralized to a pH ≈ 7 using 5M LiOH, and then the solution was added to the bottle containing preconditioned thiol-SAMMS. This mixture was then placed on a mechanical shaker for at least 24 hours. For each solution neutralized after the addition of thiol-SAMMS, the volume of Berkeley Pit water (pH ≈ 2.5) was added to the preconditioned thiol-SAMMS. This mixture was then placed on a mechanical shaker for at least 24 hours. Then, the solution was neutralized to a pH ≈ 7 using 5M LiOH.

For each solution, after the neutralization and shaking steps, a 10mL sample of the solution was taken using a 10mL syringe and filtered through a 0.45μm filter. The first 5mL were returned to the sample bottle in order to prime the filter. The remaining 5mL were added to a scintillation vial. This was repeated with a new filter to obtain 10 mL in total in the scintillation vial to be analyzed using inductively coupled plasma – mass spectrometry (ICP-MS) for mercury and ICP-optical emission spectrometry (ICP-OES) for the metals shown in Table II.

Table II: Metals tested for by the inductively coupled plasma – optical emission spectrometry (ICP-OES) instrument

Aluminum	Iron	Silver
Antimony	Lead	Sodium
Arsenic	Lithium	Strontium
Barium	Magnesium	Sulfur
Beryllium	Manganese	Thallium
Bismuth	Molybdenum	Tin
Boron	Nickel	Titanium
Cadmium	Phosphorus	Vanadium
Calcium	Potassium	Zinc
Chromium	Rhenium	Zirconium
Cobalt	Selenium	
Copper	Silicon	

The loading is a measure of the mass of a metal (in milligrams) adsorbed onto each gram of thiol-SAMMS. The equation for calculating loading is given in Equation 1,

$$Loading = ((C_i - C_f)V_{soln}) / m_{adsb} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\textbf{Equation 1}$$

where C_i and C_f are the initial and final concentrations, respectively, of the metal in solution in milligrams per liter (mg/L), V_{soln} is the volume of the solution in liters (L), and m_{adsb} is the mass

of thiol-SAMMS added to the solution in grams (g). For solutions neutralized after the addition of thiol-SAMMS, the initial concentration is that of untreated Berkeley Pit water. For solutions neutralized before the addition of thiol-SAMMS, the initial concentration is that of neutralized Berkeley Pit water.

Kinetics Experiments

A series of kinetics experiments was conducted to quantify the rate at which dissolved metals in solution adsorbed onto thiol-SAMMS. Berkeley Pit water from a depth of 750 feet was used in the kinetics experiments. Two solutions were tested: one solution was neutralized with 5M LiOH to a pH of approximately 7 before the addition of thiol-SAMMS; the other was not neutralized. The volume of each solution was measured with a volumetric flask and added to a Nalgene HDPE bottle. Each volume was verified using a four-place analytical mass balance. The ratio of Berkeley Pit water to thiol-SAMMS for each solution was 2000:1 (mL:g). Therefore, the required Berkeley Pit water volume was 1000mL and the required mass of thiol-SAMMS was 0.5g. The mass of thiol-SAMMS required for each solution was measured using a four-place analytical mass balance. The measured amount of thiol-SAMMS was added to a different Nalgene HDPE bottle and preconditioned with ethanol as described above.

Prior to starting each kinetics test, a control sample of the Berkeley Pit water solution was collected. Each experiment began when the volume of Berkeley Pit water was added to the thiol-SAMMS. Once each experiment began, samples were collected at 2, 5, 10, 15, 30, 60, 120, 240, and 480 minutes after the beginning of the experiment. During the time between sampling points, the mixtures were placed on an orbital shaker. For each sample collection time, two samples were taken. Each sample was extracted using a 10mL syringe and filtered through a 0.45μm syringe filter to remove suspended solids. For each sample, the first 5mL were returned to the sample bottle in order to prime the filter. The remaining 5mL were added to a scintillation vial. This was repeated with a new filter to obtain 10 mL in total in the scintillation vial to be analyzed using ICP-MS for mercury and ICP-OES for additional metals (Table II).
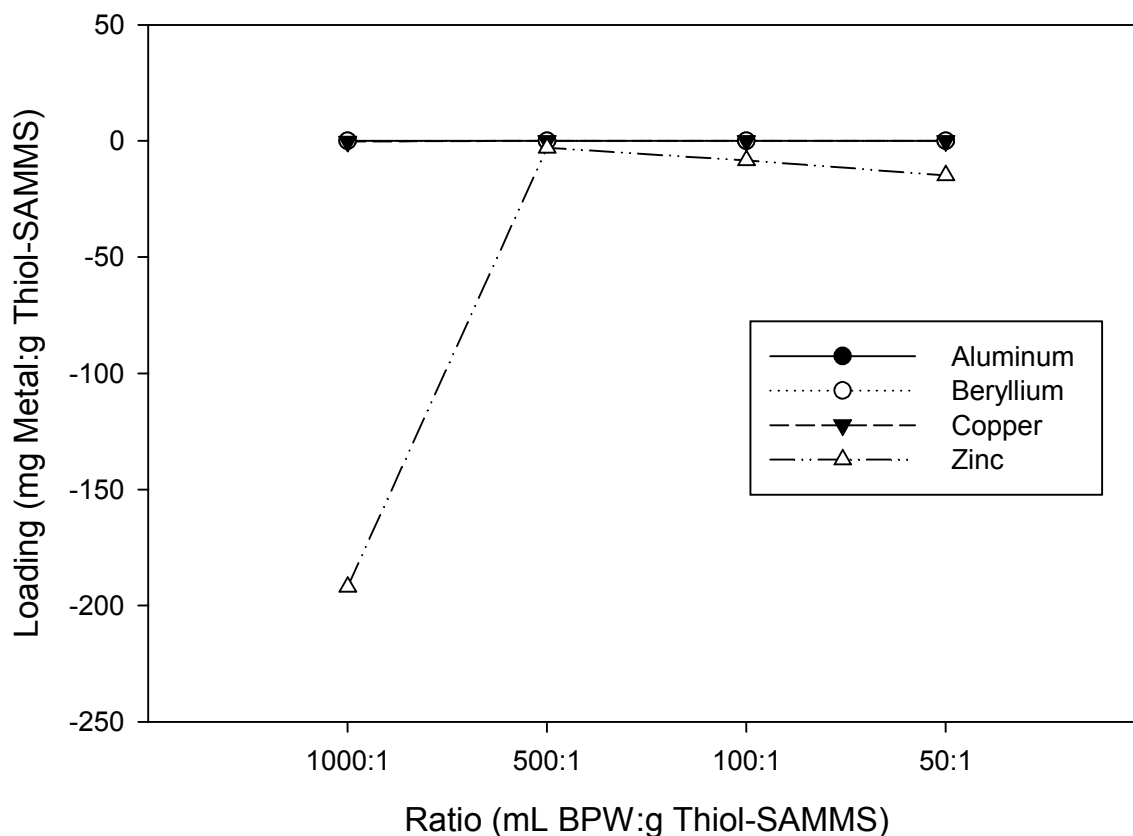
RESULTS AND DISCUSSION

Fig. 1. Loading experiment for Berkeley Pit water (BPW) from a depth of 750 feet; neutralized before addition of thiol-SAMMS

The graph in Fig. 1 displays the data for the loading experiment for Berkeley Pit water (BPW) from a depth of 750 feet, neutralized before addition of thiol-SAMMS. From Fig. 1 it can be seen that the loadings for aluminum, beryllium, and copper are near zero. This means that the initial concentration, after neutralization but before adding thiol-SAMMS, is almost equal to the final concentration, after neutralization and after adding thiol-SAMMS. Each of these concentrations, the initial and final concentrations, was measured to be near zero. This shows that the neutralization step removed the majority of these metal ions, leaving a very small amount for thiol-SAMMS to adsorb. The loading values observed for zinc are all negative, which realistically cannot occur. The remaining data must be analyzed to explain this negative loading and is discussed below.
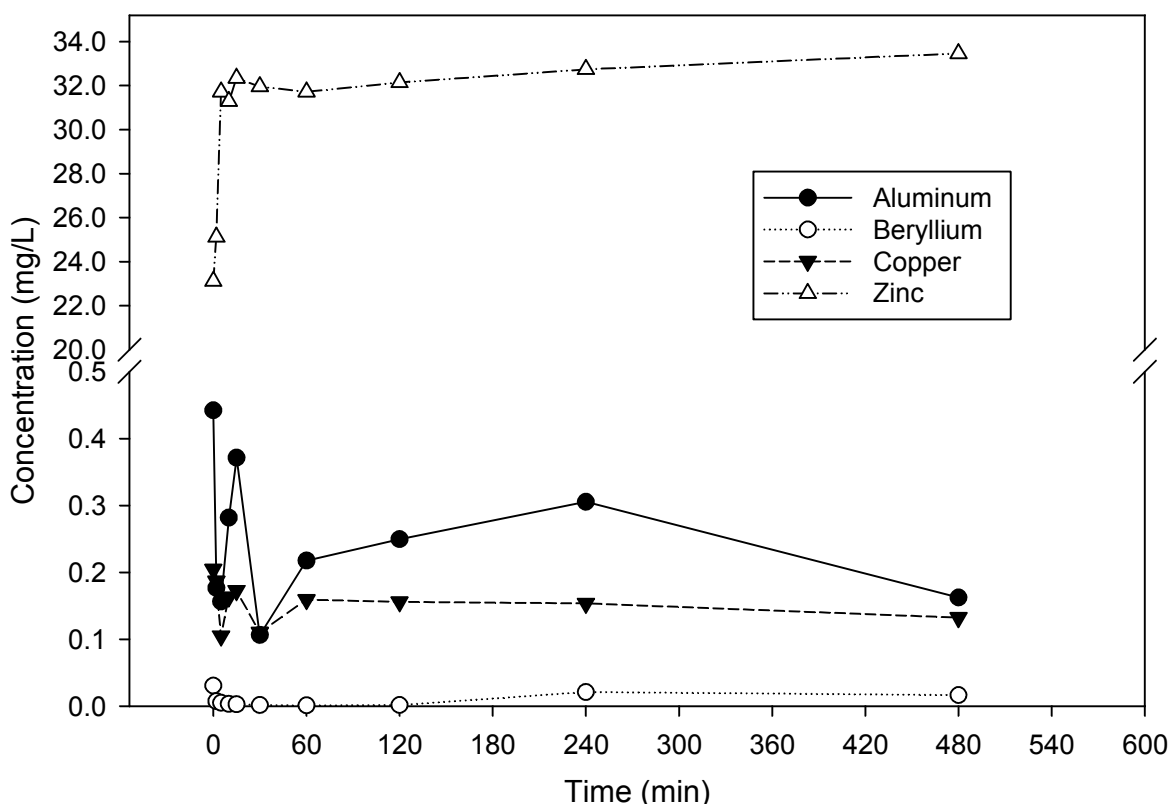
Fig. 2. Kinetics experiment for Berkeley Pit water from a depth of 750 feet; neutralized before addition of thiol-SAMMS

The graph in Fig. 2 shows the kinetics experiment for Berkeley Pit water from a depth of 750 feet, neutralized before addition of thiol-SAMMS. Fig. 2 shows that the concentrations of aluminum, beryllium, and copper fluctuate throughout the kinetics experiment. These fluctuations may have been caused by competition between the metal ions for binding sites on thiol-SAMMS. The initial concentration of each of these three metals was higher than the final concentration. For zinc, however, the initial concentration was lower than the final concentration. Zinc concentration increased over time. Because thiol-SAMMS releases hydrogen ions when metals bind to its surface [13], the hydrogen ion concentration in the solution may increase as more metals bind to thiol-SAMMS. This will cause the pH to decrease. As the pH decreases, zinc that had solidified and settled to the bottom of the solution may dissolve back into solution. This may also explain why zinc loading appears negative for Berkeley Pit water neutralized before addition of thiol-SAMMS (Fig. 1). Thiol-SAMMS may be more selective for binding to aluminum, beryllium, and copper.
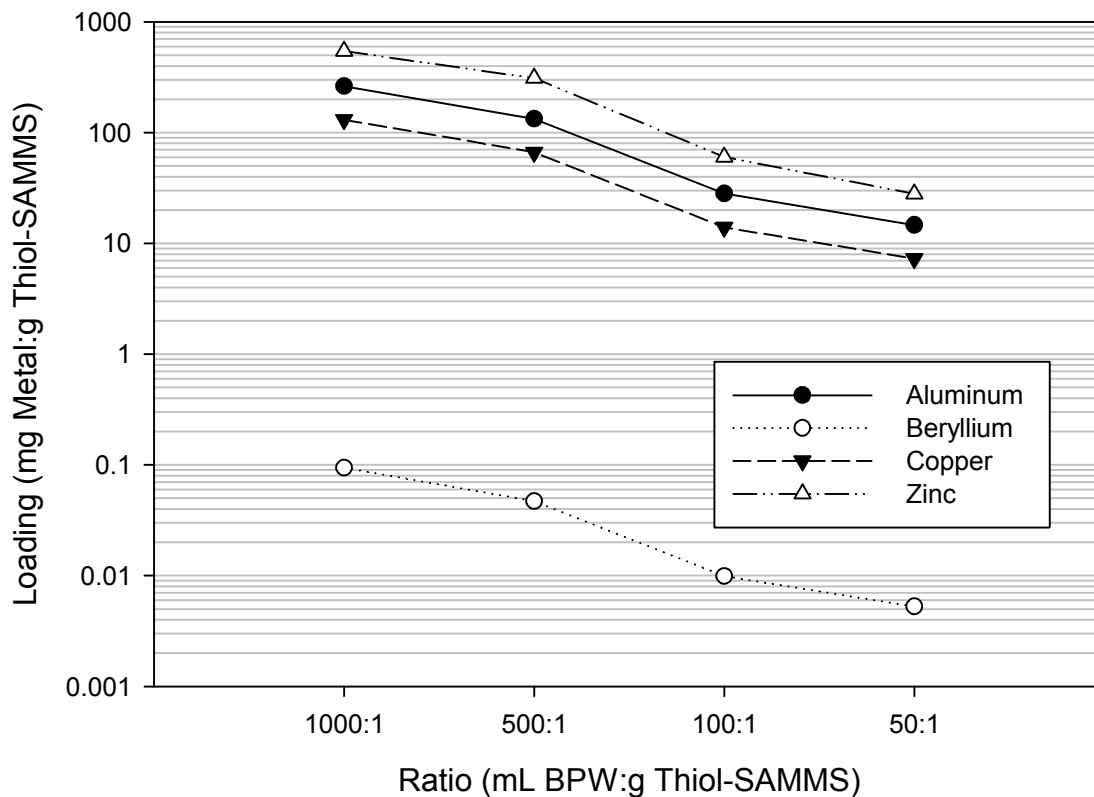
Fig. 3: Loading experiment for Berkeley Pit water (BPW) from a depth of 750 feet; neutralized after addition of thiol-SAMMS

The graph in Fig. 3 shows the loading experiment for Berkeley Pit water (BPW) from a depth of 750 feet, neutralized after addition of thiol-SAMMS. From the graph in Fig. 3, which is presented on a semi-log plot, it appears that the loading for each metal decreases proportionally with the decreasing Berkeley Pit water to thiol-SAMMS ratio. As seen in the loading experiment for Berkeley Pit water neutralized before addition of thiol-SAMMS (Fig. 1), it was determined that neutralization removes a significant amount of the dissolved metals in solution. In the loading experiment for Berkeley Pit water neutralized after addition of thiol-SAMMS (Fig. 3), it seems that the dissolved metals in solution were adsorbed onto thiol-SAMMS. However, because samples were taken only after each solution was neutralized, it is uncertain if the loadings shown in Fig. 3 were due to thiol-SAMMS adsorption or to neutralization or to both adsorption and neutralization. The remaining results must be analyzed.
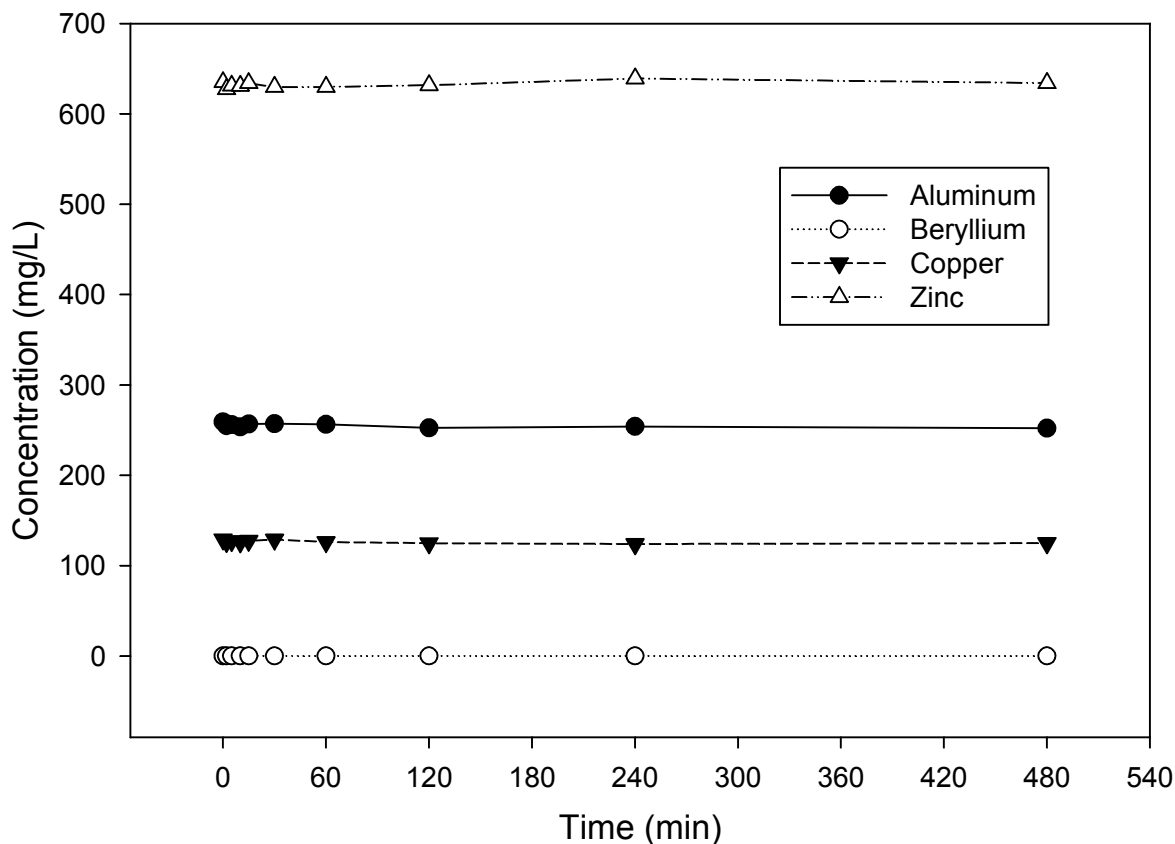
Fig. 4. Kinetics experiment for Berkeley Pit water from a depth of 750 feet; not neutralized

Fig. 4 displays the data for the kinetics experiment for unneutralized Berkeley Pit water from a depth of 750 feet. Fig. 4 shows that no changes in concentration for any of the metals were observed. Because the Berkeley Pit water is very acidic, there is a high concentration of hydrogen ions in solution. These hydrogen ions compete with metal ions in solution to adsorb onto thiol-SAMMS. In addition, because no changes in concentrations were observed in the kinetics experiment for unneutralized Berkeley Pit water (Fig. 4), the loadings observed in the loading experiments for Berkeley Pit water neutralized after the addition of thiol-SAMMS (Fig. 3) were likely due to neutralization and not metal loading onto thiol-SAMMS.

Table III: Summary of concentrations of contaminants in Berkeley Pit water (BPW) and maximum contaminant levels (MCLs) of each contaminant, as well as detection limits for the inductively coupled plasma – mass spectrometry (ICP-MS) and ICP – optical emission spectrometry (ICP-OES) instruments

Compound	Ratio of Berkeley Pit water to Thiol-SAMMS (grams BPW : grams Thiol-SAMMS)	ICP-MS and ICP-OES Detection Limit (mg/L)	MCL (mg/L)	Initial Concentration in Berkeley Pit water (mg/L)	Concentration after neutralization, before adding Thiol-SAMMS (mg/L)	Concentration after neutralization and adding Thiol-SAMMS (mg/L)
Aluminum	1000:1	0.01647	0.2	262.951	0.169	0.203
	500:1					0.194
	100:1					0.266
	50:1					1.140
Beryllium	1000:1	0.00237	0.004	0.105	0.018	0.022
	500:1					0.018
	100:1					0.007
	50:1					0.016
Copper	1000:1	0.0087	1.3	130.935	0.166	0.467
	500:1					0.155
	100:1					0.255
	50:1					0.328
Zinc	1000:1	0.0299	5	653.548	2.638	193.734
	500:1					8.567
	100:1					81.756
	50:1					266.182

Table III presents the results from loading experiment neutralized before addition of Thiol-SAMMS. Table IIITable III shows that neutralization alone decreases the concentrations of aluminum, copper, and zinc to concentrations below the MCL of each these three metals. The beryllium concentration significantly decreases after neutralization, but not enough to meet drinking water standards. Each concentration in Table III represents a concentration taken at one particular time. Fig. 2 shows that the concentrations of aluminum, beryllium, and copper fluctuate over time. Thus, the concentrations shown in Table III may not be equilibrium concentrations; rather, the aqueous concentrations are likely influenced by dissolution-precipitation reactions of secondary solids that formed during neutralization.

The addition of thiol-SAMMS, after neutralization of Berkeley Pit water, had inconsistent effects for each of the four metals tested. For aluminum, concentration increases at all four ratios. For beryllium, concentrations increase at a ratio of 1000:1, are constant at a ratio of 500:1, and decrease at ratios of 100:1 and 50:1. For copper, concentrations decrease at a ratio of 500:1 and

increase at ratios of 1000:1, 100:1, and 50:1. For zinc, the aqueous concentration increases over all ratios investigated. Thus, it is postulated that neutralization of the solution prior to addition of thiol-SAMMS results in the formation of secondary phases and it is the dissolution-precipitation of these phases that is resulting in the apparent inconsistent removal of aqueous metals by thiol-SAMMS.

Additionally, solid metal species that formed after neutralization were left in all the loading and kinetics test solutions. Thus, it is possible that metals in the solid phase dissolved back into solution after addition of thiol-SAMMS. Hydrogen ions are released as thiol-SAMMS binds with dissolved metals. As hydrogen ion concentration increases, solid metal species may dissolve back into solution.

CONCLUSIONS AND FUTURE WORK

A large amount of the dissolved metals in Berkeley Pit water can be removed by neutralization. The combination of neutralization followed by thiol-SAMMS sequestration could reduce contaminant levels to below drinking water standards. Future research is necessary to more thoroughly evaluate the results presented here. In particular, a set of loading and kinetics experiments should be run wherein the solids, which are formed after neutralization, are removed before adding thiol-SAMMS. This would allow for metals to adsorb onto thiol-SAMMS without the potential for metals from the solid phase dissolving back into solution. This set of experiments would help determine how thiol-SAMMS can further reduce dissolved metal concentrations in neutralized Berkeley Pit water.

In the kinetics experiment for Berkeley Pit water neutralized before the addition of thiol-SAMMS, the majority of dissolved metals formed solids that settled to the bottom of the bottle. These solids were not removed from the bottle. This may have caused solid zinc species, and possibly other solid metal species, to dissolve back into solution upon addition of thiol-SAMMS. When thiol-SAMMS bonds to metal ions, it releases hydrogen ions, which may decrease the pH of the solution. It is this drop in the pH which may have been the reason that zinc dissolved back into solution. From the results, it seems that thiol-SAMMS is more selective for binding to aluminum, beryllium, and copper, but more research is necessary to determine for which metals thiol-SAMMS is most selective.

Future work can include a set of loading and kinetics experiments where the solid phase is removed once the solution is neutralized. This would simplify the processes inside the solution by removing secondary phases, such as solids formed after neutralization. This would also allow for an understanding of whether or not increased dissolved metal concentration upon addition of thiol-SAMMS, as in the case of zinc in this research, was caused by dissolution of secondary phases. Additionally, results indicate that there may be competition between metal ions for binding sites on thiol-SAMMS. Experiments can be designed to test two metals at a time, then more, to determine competition between different metals for binding sites onto thiol-SAMMS. In addition, thiol-SAMMS may be added to a computer model to help understand how metal loading onto thiol-SAMMS is affected under different conditions. If the computer model is reliable and has been tested and verified for numerous conditions with known concentrations, a better understanding of metal loading onto thiol-SAMMS can be achieved.

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