

Novel Pb^{2+} -Complexing Cryptand-Functionalized Vinyl Polymer for Hydrological Remediation

Project Summary

1 Introduction

1.1 Overview and Significance

Lead(II) (Pb^{2+}) is a widespread and pervasive environmental contaminant in marine, lacustrine, and anthropogenic water systems. Despite centuries of research documenting the adverse health effects of lead exposure, it remains a critical and persistent public health issue, with one of three children worldwide having potentially harmful blood lead levels.

This research proposes the design and synthesis of a novel and non-toxic polymer consisting of a water-soluble crosslinked polyvinyl alcohol (PVA) backbone with cryptand side chains capable of selective and reversible Pb^{2+} ion complexation. The proposed Pb^{2+} -Complexing Cryptand-Functionalized Vinyl Polymer (PbCVP) leverages the environmental compatibility and scalability of PVA-based materials alongside the high binding affinity and ion selectivity of cryptands for the remediation of hydrological remediation. Furthermore, the reversible host-guest interactions enable the regeneration of PbCVP for future use, making its implementation sustainable and cost-effective for long-term hydrological remediation.

PbCVP could provide an effective, scalable, and environmentally sustainable solution to lead contamination in natural and anthropogenic water systems, addressing a major challenge in hydrological remediation and public health.

1.2 Program Relevance

The design and synthesis of PbCVP aligns with several aims listed by the Critical Aspects of Sustainability: Innovative Solutions to Sustainable Chemistry (CAS-SC) program. The project offers an interdisciplinary solution to lead pollution in water, coalescing host-guest chemistry with polymer science by functionalizing the PVA backbone with cryptand side chains. The synthesis of PbCVP is energy efficient and scalable, making it a practical option for large-scale decontamination. Unlike a variety of existing hydrological remediation methods, reversible binding enables the reuse of PbCVP, minimizing material waste and manufacturing demands. The ability for continued use due to this regenerative property therefore makes PbCVP a circular technology.

This innovative approach provides an efficient and environmentally friendly method for the decontamination of hydrological systems while invoking the principles of a circular economy by optimizing resource efficiency and waste reduction.

1.3 Background and Motivation for Research Plan

1.3.1 Lead and Public Health

Lead is well-documented to leach off of pipes, faucets, fixtures, and lead-based solder in water-distribution networks. In the U.S. alone, approximately 22 million people drink from full or partial lead pipe systems [4]. The World Health Organization has estimated lead poisoning is responsible for 30% of idiopathic intellectual disability, 4.6% of cardiovascular disease and 3% of chronic kidney diseases. Efforts have been made towards the replacement of lead piping and

solders, yet, the high cost of uprooting and reinstalling hydrological infrastructure disproportionately exposes lower income communities and developing countries to more lead.

Alarming, UNICEF has estimated that one third of children worldwide have blood lead levels (BLL) above 5 $\mu\text{g/dL}$, which the World Health Organization has concluded to inflict adverse health affects [1]. Lead poisoning is particularly detrimental to children, as an estimated 3.9-7.4 IQ points are lost as a child's BLL increases from 1 to 10 $\mu\text{g/dL}$, and recent studies have proven that even levels as low as 3-4 $\mu\text{g/dL}$ lead to poor educational outcomes. This loss is estimated to reduce total lifetime earnings by \$165-233 billion and lead exposure as a whole has cost the U.S. alone more than \$50 billion in lost lifetime productivity [6]. Lead exposure and poisoning is demonstrably one of the most prevalent and pressing public health issues globally, thus, it is critical that sustainable remediation efforts are implemented in anthropological water systems.

1.3.2 Lead and the Environment

Lead is also an increasingly prevalent contaminant in marine and lacustrine systems. Flint, Michigan, a former industrial hub for manufacturing, lead levels in water are as high as 0.0252 mg/L in 95% of samples, a concentration far above what the Environmental Protection Agency determined to be a concerning level (0.015 mg/L) [10]. Furthermore, in the Northeast Pacific, concentrations of lead are roughly tenfold higher in surface and thermocline waters than deep waters, indicating high levels of anthropogenic lead input [9]. Chronic lead exposure has been proven to inhibit metamorphosis, disrupt neurology and immune responses, and impair developmental processes in aquatic organisms. Sea urchins, which provide a commonly used model for evaluating the toxic effects of metal pollution, had reduced offspring quality due to lead exposure [7]. Furthermore, lead concentrations will be further elevated in animals higher on the food chain due to biomagnification, which may lead to the improper development or toxicity in ecologically critical predators. This further affects humans that regularly consume or rely on marine or lacustrine organisms. It is evident that lead contamination is harmful to marine and lacustrine systems and the organisms that reside in them.

1.3.3 Polyvinyl Alcohol

PVA is commonly employed as a polymeric membrane for treating water (e.g. desalination, wastewater treatment) due to its water-solubility, non-toxicity, thermal and mechanical stability, and biodegradability. These properties have made PVA an emerging candidate for the replacement of traditional plastic films, as recent studies have demonstrated how microorganisms facilitate the break down of PVA into water and carbon dioxide [3].

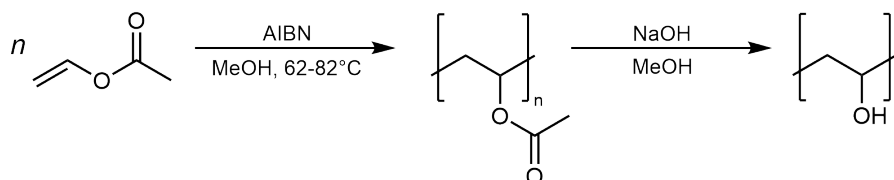


Figure 1: Reaction scheme for the synthesis of PVA.

The synthesis of PVA proceeds via the hydrolysis of polyvinyl acetate (PVAc), which is radically polymerized with vinyl acetate. PVAc is widely commercially available and can be bought at relatively low prices, enabling PbCVP to be synthesized in less steps and more cost-effectively. The abundance of hydroxyl groups makes PVA readily soluble in water so the polymer chains will be densely crosslinked to prevent dissolution in water, as well as enhance mechanical properties. This would make its supramolecular architecture comparable to a hydrogel, thus it may exhibit the same mechanochemical autonomous repair. This is especially advantageous in the context of

remediation in non-anthropogenic hydrological systems, where debris or organisms may damage PbCVP. Due to the abundance of hydrogen bonding between alcohols, PVA exhibits semi-crystalline properties but has flexible polymer chains due to freely rotating C-C bonds. This flexibility increases the accessibility of the cryptand side chains to any free Pb^{2+} ion. Finally, the hydroxyl groups will be able to interact with a variety of other ions present in hydrological systems that may compete with Pb^{2+} such as Na^{2+} , Ca^{2+} , Mg^{2+} , and Fe^{3+} .

1.3.4 Cryptands

Cryptands are discrete multidentate macropolycyclic ligands with a three-dimensional interior cavity that selectively coordinates with charged species (prototypically cations) through intermolecular interactions from donor atoms.

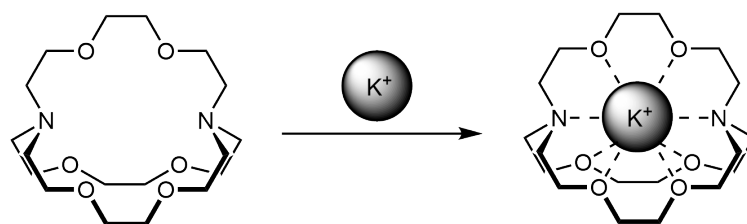


Figure 2: Complexation of a potassium ion by [2.2.2]cryptand.

Several structural and chemical components improve cryptand metal ion selectivity, including: i) donor atoms with a high affinity for the ion; ii) size-match relationship: cavity diameter matching the ionic radius of the metal; and iii) symmetry for a uniform binding environment. Recent advances in supramolecular chemistry have led to the development of water-soluble coordination cages for heavy metals and cryptands capable of the host-guest complexation of heavier elements such as lanthanides.

2 Research Plan

2.1 Objectives

The three aims of this project include the synthesis and functionalization of the PbCVP backbone, the optimization of Pb^{2+} selectivity and binding, and the fine-tuning of PbCVP crosslinking and physicochemical properties.

The synthetic pathway of PbCVP will be designed to maximize efficiency, scalability, environmental friendliness, and yields. Thus, the reactions will be reliable and deploy reagents that can be bought in bulk for scaling of PbCVP for large-scale hydrological remediation projects. The cryptand side chains will also be optimized to complex Pb^{2+} ions while maintaining reversibility so PbCVP can be reused. This involves the selection of donor atoms based on Hard and Soft Acid and Base (HSAB) Theory and the geometry, cavity diameter, and conformation of the cryptand structure and supramolecular architecture. Finally, the selection of the crosslinking agent and adjustment of the side chain density must be determined for increased accessibility of cryptand binding sites and overall polymer stability.

2.2 Experimental Plan

Aim 1: Synthesis

PVAc will act as the starting material for the synthesis of PbCVP. The addition of PVAc into a solution of sodium hydroxide in methanol will hydrolyze PVAc into PVA. Both aforementioned

reagents are common and affordable, enabling this hydrolysis to be upscaled. Due to the flexible nature of PbCVP, the deployment of a stereospecific catalyst is not necessary, thus, the polymer will be atactic. Then, a benign oxidation method developed by Wang et al. will be implemented to transform the PVA into partially oxidized PVA and polyketone, using *para*-toluenesulfonic acid (pTSA) in 30% aqueous hydrogen peroxide at 90°C. At 24 hours, roughly 50% of hydroxyl groups have been converted to ketones [11]. This enables the fine-tuning of cryptand side chain density, as a ketone is necessary for the addition of the alkyne handle. The benign nature of this oxidation also keeps the manufacturing of PbCVP relatively environmentally friendly.

N-Bromosuccinimide (NBS) and acetic acid will be used for α -bromination. Acetic acid is deployed to enolize the ketone, enabling NBS to brominate the α -carbon. Both reagents are financially accessible and NBS is an especially reliable alternative to Br_2 . Then, monosodium acetylide, which is prepared by deprotonating acetylene with sodium amide, is added to attach the alkyne to the α position via $\text{S}_\text{N}2$. Monosodium acetylide is chosen instead of lithium acetylide for cost reasons. The polymer is added to a solution of sodium borohydride in ethanol to reduce all ketones to alcohol groups. Sodium borohydride is selected as the hydride donor as it is mild enough to not protonate the alkyne. The acid workup is carried out with 1M hydrochloric acid, which is dilute enough to not disrupt the alkyne handle.

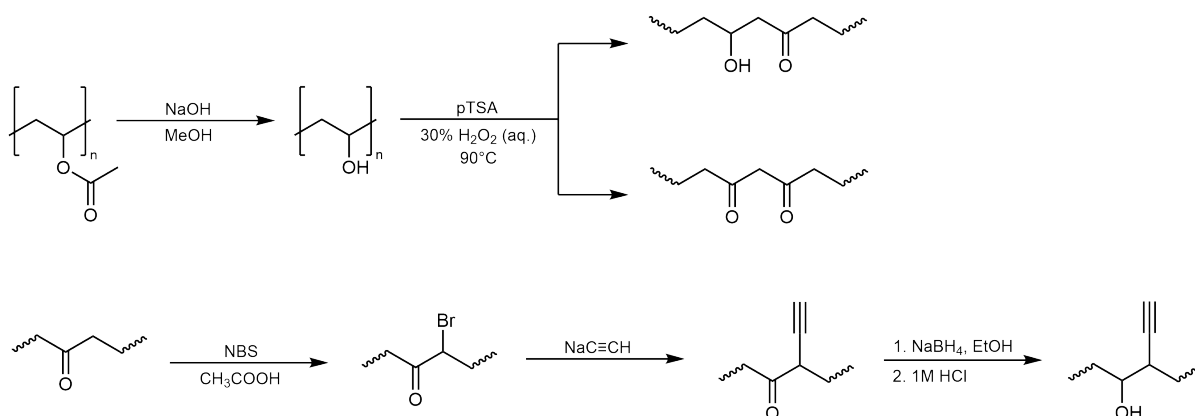


Figure 3: Reaction scheme for the synthesis of PbCVP polymer chains.

The novel Pb^{2+} -Complexing Cryptand (PbCC) is attached to an azide which reacts with the alkyne when the copper catalyst is added. Due to the risk of the copper being oxidized, the reaction will proceed under an inert dinitrogen atmosphere. The copper-catalyzed azide-alkyne cycloaddition (CuAAC) is a commonly employed click reaction, a class of reactions designed to link molecules and known for their high favorability, stereospecificity, regioselectivity, modularity, and high yields. The reaction generates a 1,4-disubstituted triazole linkage between the PVA backbone and PbCC, which contains nitrogen heteroatoms that would be able to interact with other ions that may compete with Pb^{2+} for complexation.

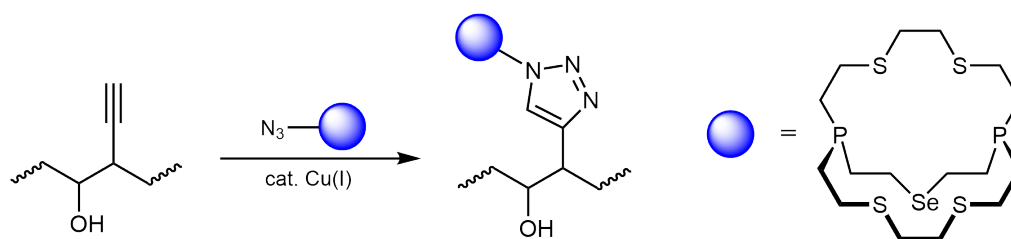


Figure 4: Reaction scheme for the addition of PbCC to PbCVP polymer chains.

Aim 2: Optimization of Pb^{2+} Complexation

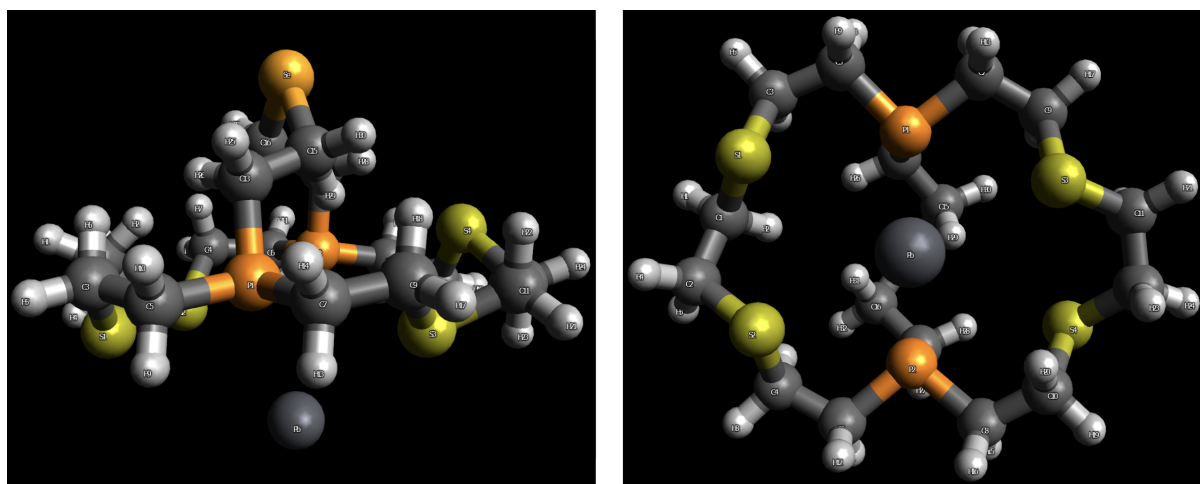


Figure 5: Simulated complexation of a Pb^{2+} ion by [4S, 1Se, 2P]-PbCC.

Hard and Soft Acid and Base (HSAB) Theory is employed as the basis for the selection of donor atoms that could optimize the complexation of Pb^{2+} ions. HSAB Theory posits that acids and bases can be categorized as “hard” and “soft” based on polarizability, charge density, and tendency to form covalent vs. ionic interactions. Pb^{2+} is classified as a borderline soft acid. Soft acids and bases are characterized by their high polarizability, low charge density, and tendency to form covalent bonds. Following the general principle of “like-likes-like”, soft acids and bases tend to attract and form interactions with one another. Soft-soft interactions have strong covalent character because soft acids and bases have similar orbital energies. This can be attributed to the quantum mechanical particle-in-the-box model, which posits that the smaller the “box” (i.e. atomic orbitals), the wider the gap between energy states. Therefore, soft acids and bases, which have more diffuse electron clouds (lower charge density), are statistically more likely to have lowest unoccupied molecular orbitals and highest occupied molecular orbitals that are close to one another in energy, giving rise to their covalent character.

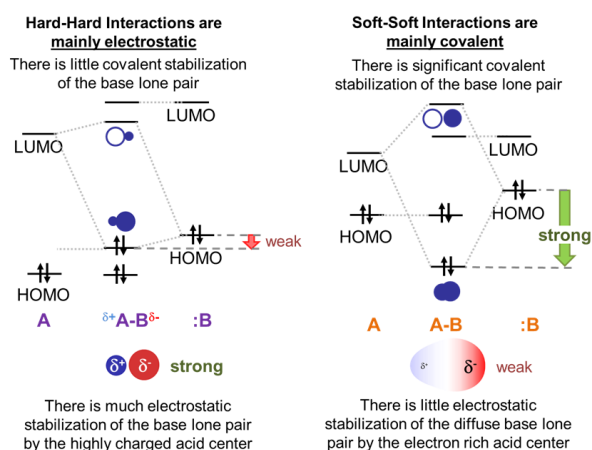


Figure 6: Reproduced from LibreTexts (accessed on December 10, 2024).

While cryptands typically incorporate a mix of oxo- (R_2O) and amino- (R_3N) ligands, both fall under the hard base category. To optimize the donor atoms in accordance to the principles of HSAB Theory, thio- (R_2S), seleno- (R_2Se), and phospho- (R_3P) ligands have been selected for PbCC. Furthermore, thio- and seleno- ligands have been experimentally proven to have a higher affinity for Pb^{2+} when compared to oxo- and amino- ligands [5]. The hydrocarbon framework is based on [2.2.1]-cryptand, which is able to complex Hg^{2+} , a soft acid with a similar ionic radius

to Pb^{2+} [2]. The supramolecular architecture of [2.2.1]-cryptand sterically accommodates Pb^{2+} and contains internal planes of symmetry.

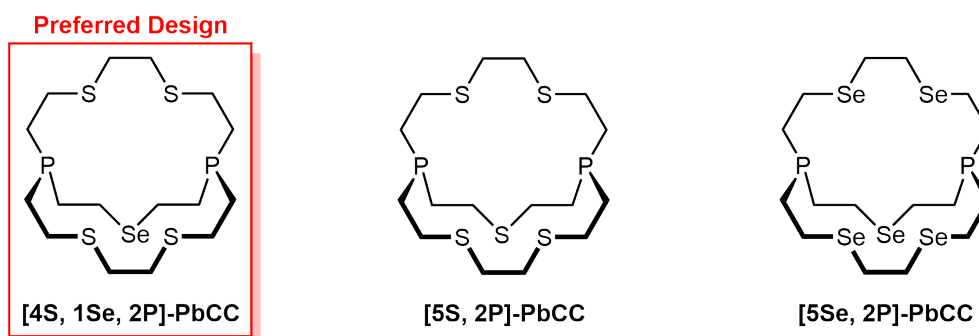


Figure 7: Designs for PbCC (Pb^{2+} -Complexing Cryptand).

[5S, 2P]-PbCC and [5Se, 2P]-PbCC (Figure 7) reflect opposite ends of a spectrum, with different advantages in different areas. [5S, 2P]-PbCC is more environmentally benign, purely consisting of heteroatoms that can be found in biological systems. [5Se, 2P]-PbCC has a superior affinity for Pb^{2+} due to its selenoligands, which are softer than thioligands. However, selenium is a toxic environmental contaminant and organoselenium compounds are more costly which makes scaling the synthesis of PbCVP more challenging. Damage to PbCVP is always a possibility during its deployment in marine or lacustrine hydrological systems so it may be counterintuitive to risk introducing a different metal contaminant while capturing Pb^{2+} . [4S, 1Se, 2P]-PbCC remains mostly environmentally benign while having the highly soft selenoligand in the bridge-head, which is an optimal position for drawing a free Pb^{2+} ion into the cavity of the cryptand.

[4S, 1Se, 2P]-PbCC with a free Pb^{2+} ion was rendered in with its optimal molecular geometry using Avogrado and the calculated net force (represented by a green vector arrow) acting upon the Pb^{2+} ion is evidently towards the interior cavity of the cryptand (Figure 8).

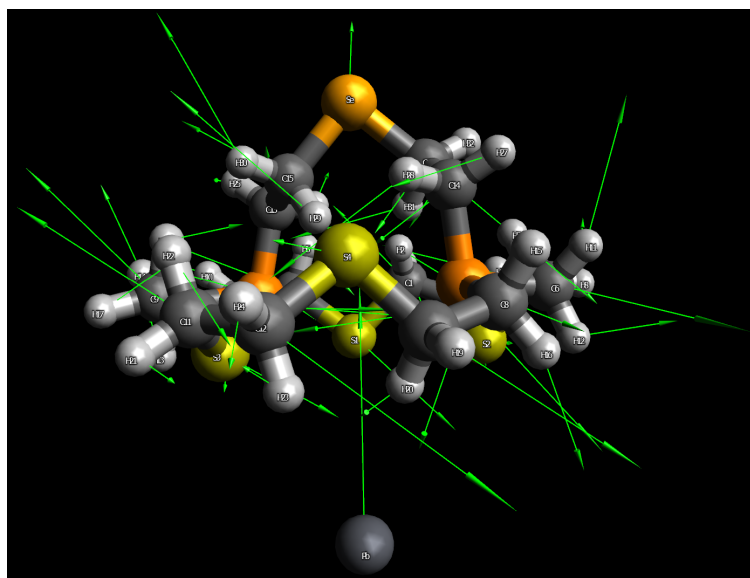


Figure 8: Simulation of net forces acting on [4S, 1Se, 2P]-PbCC and a Pb^{2+} ion.

The electrostatic potential of [4S, 1Se, 2P]-PbCC and a complexed Pb^{2+} ion was also mapped (Figure 9). The [4S, 1Se, 2P]-PbCC- Pb^{2+} complex is noticeably polarized, with electron density localized around the Pb^{2+} ion and cryptand interior while the cryptand exterior remains mostly electron deficient. In line with HSAB Theory, the focused electron density invokes its covalent

character which is characteristic of soft-soft interactions. The electron-poor exterior decreases the chances of a different metal cation interacting with the [4S, 1Se, 2P]-PbCC once it has complexed Pb^{2+} , reducing the chances of competitive binding.

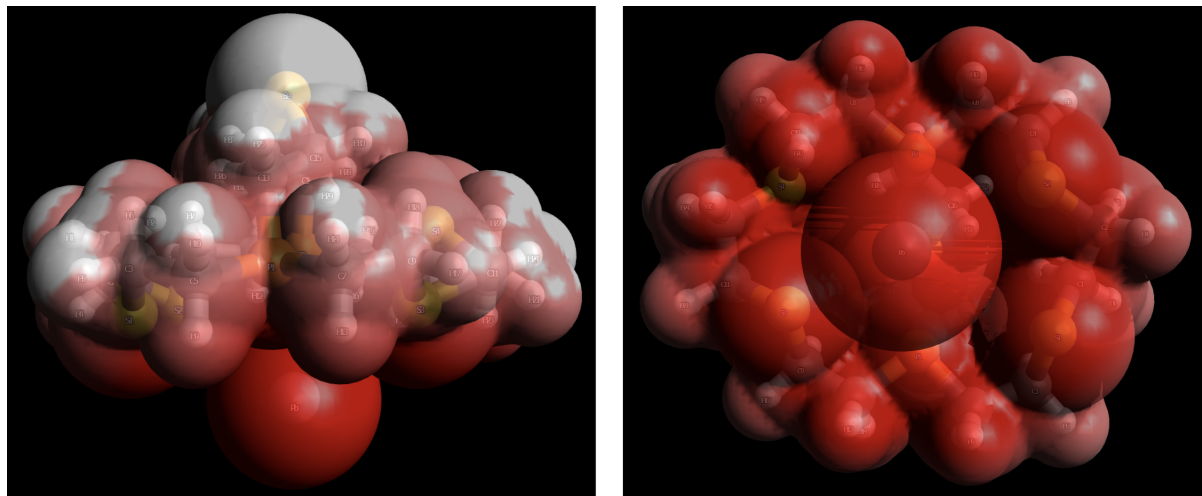


Figure 9: Simulated electrostatic potential surface of a [4S, 1Se, 2P]-PbCC- Pb^{2+} complex.

It is important to note that Pb^{2+} is intentionally bound in an *exo* manner (wherein the ion is not entirely inside of the cavity) to enhance reversible binding. A majority of other metal ions present in hydrological systems that may compete with Pb^{2+} , such as Na^{2+} , Ca^{2+} , K^{+} , Mg^{2+} , Fe^{3+} , Mn^{2+} , and As^{3+} , are hard acids that would preferentially interact with the surrounding hard bases such as H_2O and the -OH on the PVA backbone. Other soft acids that are present in waters are often found at trace amounts or are also toxic heavy metal contaminants (i.e. Hg^{2+} , Cd^{2+} , Cu^{2+} , and Ag^{+}), thus, their complexation would be sparse and remain beneficial for the environment.

The strength of the complexation will be experimentally determined using real-time ^1H Nuclear Magnetic Resonance (^1H NMR) spectroscopy and ^1H -1D Exchange Spectroscopy (EXSY) with PbCVP in conditions meant to simulate anthropogenic, marine, or lacustrine hydrological systems. Pb^{2+} is tightly bound if the NMR spectra reflects a slow exchange, where the complexed and uncomplexed states of the cryptand appear as distinct sets of peaks. Weaker binding results in a fast exchange, where the ion rapidly shifts between its free and bound state which is reflected by a single averaged peak on the NMR spectra.

Aim 3: Crosslinking & Physicochemical Properties

Crosslinked polymers exhibit enhanced mechanical resilience, thermal stability, and separation capabilities. The crosslinking in PbCVP will be optimize its physicochemical properties to weather anthropogenic, marine, and lacustrine hydrological systems as well as bolster the accessibility of cryptand binding sites to maximize Pb^{2+} ion complexation.

Linkages formed by the introduction of a crosslinking agent can be broadly classified into two categories: covalent and physical linkages. Covalent linkages result in the formation of formal bonds between polymer chains, this may alter the functionality such as in the case of PVA with succinic acid (SA) where the alcohol groups are converted for an ester linkage through hydrolysis, generating water molecules as a byproduct. Physical linkages leverage intermolecular forces (e.g. Van der Waals forces, ionic interactions, dipole-induced dipole interactions, etc.) which are reversible. Borax is a commonly employed physical crosslinking agent that forms hydrogen bonds with two adjacent hydroxyl groups on each PVA polymer chain (Figure 10).

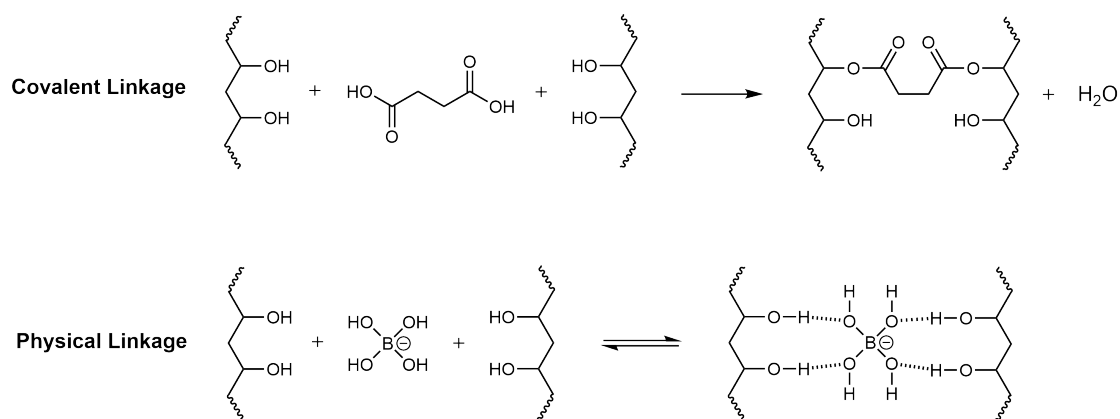


Figure 10: Crosslinking of PVA with SA (covalent linkage) vs. borax (physical linkage).

A covalent crosslinker will be selected for the crosslinking of PbCVP PVA polymer chains. The swelling that would occur when PbCVP is submerged in water due to water molecules forming hydrogen bonds with the PVA hydroxyl groups, coupled with the bulky [4S, 1Se, 2P]-PbCC side chains, necessitate strong irreversible linkages between polymer chains to prevent dissolution in aqueous environments. Covalent linkages ensure long-term stability, allowing PbCVP to maintain its structural integrity against mechanical and thermal stress or changes in pH which may occur in non-anthropological hydrological systems.

In recent years, a diverse array of covalent crosslinking agents have been developed for PVA. When examining these crosslinking agents, two structural motifs arise for the crosslink: the linkage either connects to a single atom or multiple atoms on each of the polymer chains. For example, terephthalic acid (TPA) generates an ester linkage from one alcohol group per polymer chain. On the other hand, the introduction of a dialdehyde such as glutaraldehyde (GA) results in the formation of a hemiacetal which links two alcohol groups per polymer chain. Single-site linkages offer superior flexibility, a greater degree of swelling, and minimal steric hinderance while multi-site linkages offer rigidity, mechanical resilience, and thermal stability.

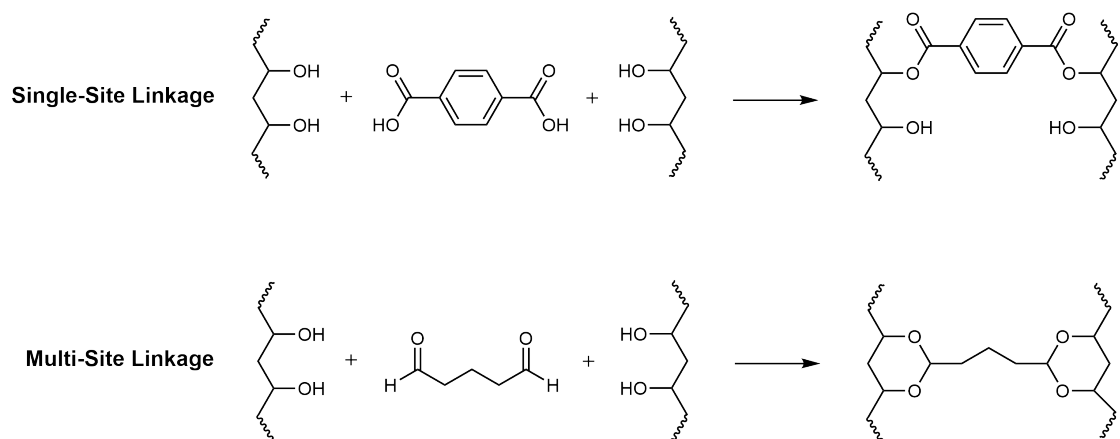


Figure 11: Crosslinking of PVA with TPA (single-site linkage) vs. GA (multi-site linkage).

A single-site crosslinking agent will be selected for the crosslinking of PbCVP PVA polymer chains. Flexibility is important for the functionality of PbCVP as it increases the accessibility of cryptand binding sites by allowing greater rotational freedom and range of motion of individual chains. Swelling further increases the ease of access to [4S, 1Se, 2P]-PbCC as more space is present between polymer chains, increasing the probability for Pb^{2+} ions to flow in and be

complexed. While multi-site linkages can conveniently arrange PbCVP into a high-performance membrane, which is a more manageable form for hydrological remediation, it is less optimal for Pb^{2+} complexation. PVA crosslinked with 4% GA had a 19% reduction in water solubility and resulted in 100% less swelling [8].

The requirement for crosslinking agents to form a covalent and single-site linkage narrows down the selection of PVA agents to several dicarboxylic acids and dianhydrides (Figure 12).

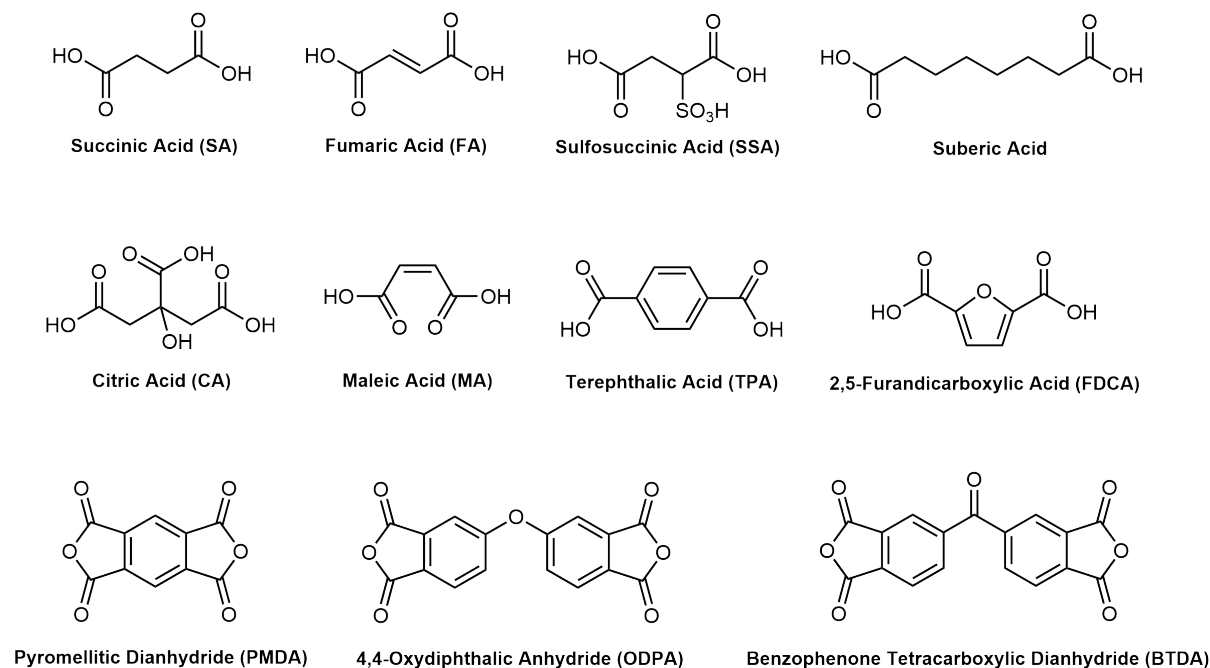


Figure 12: Covalent single-site PVA crosslinking agents.

Citric acid and suberic acid offer distinct advantages. Citric acid is environmentally benign as it is a common natural product, scalable due to its financial accessibility, and offers multiple polar sites (two esters, a carboxylic acid, and an alcohol) that enhance swelling and increase interactions with hard acid metal ions. The linkage formed by suberic acid spans eight atoms, providing significant spacing for water and free ions between polymer chains while avoiding the steric bulk associated with dianhydride crosslinking agents. However, suberic acid contains a central hydrocarbon segment which is nonpolar and hydrophobic in nature. Such hydrocarbon chains are also reminiscent of traditional plastics, which is counterintuitive to the biodegradable design of PbCVP. Furthermore, suberic acid is significantly more expensive than citric acid which diminishes the scalability of the production of PbCVP. Citric acid offers an ecofriendly and inexpensive option for crosslinking that further enhances the properties of PbCVP that increase its ability to maximally complex Pb^{2+} ions.

The density of [4S, 1Se, 2P]-PbCC side chains on polymer chains can be fine-tuned during the oxidation step following the hydrolysis of PVAc. At 90°C, 50% of alcohol groups were converted to ketones after 24 hours [11]. The ketone is necessary for the functionalization of the α -carbon by alkyne handles. Therefore, the temperature and reaction duration can be manipulated to precisely adjust the amount of [4S, 1Se, 2P]-PbCC side chains relative to the amount of alcohol groups on the backbone. [4S, 1Se, 2P]-PbCC and the triazole unit resulting from the click reaction possess significant steric bulk lowers the crystallinity of the polymer as they hinder packing of polymer chains. Thus, the citric acid crosslinking is crucial for the structural integrity and mechanical resilience of PbCVP. The porosity and semi-crystalline (possibly bordering on amorphous) nature of PbCVP may necessitate attaching it to a rigid and flat structure that

remains soluble enough to allow for the passage of water and metal ions. Such a substrate would ensure mechanical stability and provides structure for ease of implementation into hydrological systems.

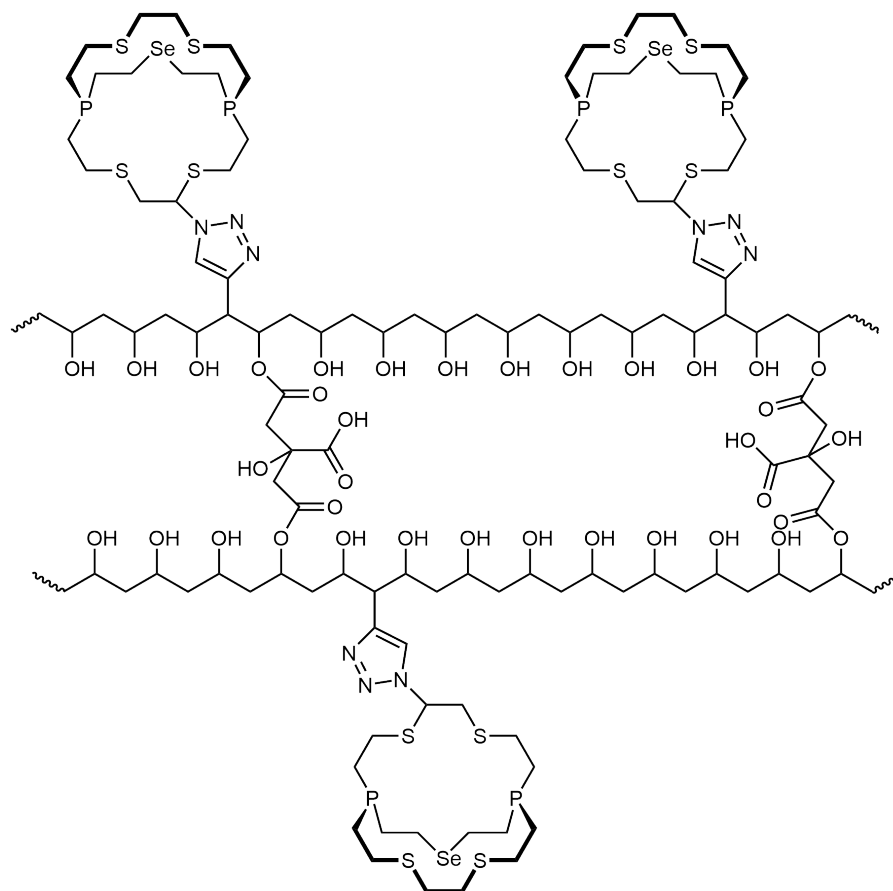


Figure 13: Segment of PbCVP after crosslinking with citric acid.

3 Intellectual Merit

This project bridges the fields of host-guest chemistry and polymer science to address a major problem environmental problem. PbCVP synergizes the exceptionally strong ion complexing capabilities of cryptands with a veratile, water-soluble, and ecofriendly polymer backbone. Furthermore, PbCVP leverages HSAB Theory to optimize the selectivity of the cryptand, incorporating donor atoms that are less commonly employed by existing cryptands. The implementation of cryptands for selectively binding and removing toxic heavy metal contaminants is fully realized with the PVA backbone, which is designed to be porous enough for water and ions to pass through. The project also adheres to the sustainable principles of green chemistry through reversible binding which enables the regeneration and reuse of PbCVP.

4 Broader Impacts

The broader impacts of this project extend across public health and environmental remediation. Lead contamination in anthropogenic hydrological systems poses neurological, cardiovascular, and renal health problems worldwide. While indirectly, lead exposure significantly reduces productivity on national scales, as the intellectual disabilities and reduction in IQ caused by lead poisoning negatively affects educational and professional performance. Furthermore, lead

poisoning disproportionately affects low-income communities and third world countries where resources for infrastructure replacement are limited. This project addresses this inequity with its scalability and circular nature. The reusability of PbCVP is important for its implementation in poorer communities and diverges from the typical, predatory models that require such communities to repeatedly purchase products. This invokes the principles of a circular economy, reducing waste and resource consumption as manufacturing does not need to be scaled to the degree of a single-use product. The synthesis of PbCVP is also mostly environmentally benign, further reducing its environmental footprint.

This project presents an sustainable and cost-effective solution to lead contamination in hydrological systems while fostering collaboration at the intersection of supramolecular chemistry, polymer science, and environmental science.

5 References

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