University of Massachusetts Amherst

ScholarWorks@UMass Amherst

Environmental & Water Resources Engineering
Masters Projects

Civil and Environmental Engineering

Winter 1-2017

Effects of Sulfidation on the Deposition and Detachment of Silver Nanoparticles

Joseph Murphy

Follow this and additional works at: https://scholarworks.umass.edu/cee_ewre

Part of the Environmental Engineering Commons

Effects of Sulfidation on the Deposition and Detachment of Silver Nanoparticles

Joseph Murphy

Submitted to the Department of Civil and Environmental Engineering of the University of Massachusetts in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE IN ENVIRONMENTAL ENGINEERING

May 2017

Acknowledgements

I would like to gratefully thank my advisor Dr.Boris Lau for the opportunity to be part of the continuing effort of research he has committed to and for his guidance and support over the years. I would also like to thank Dr. John E. Tobiason for sitting on my committee and being a valuable mentor during my time here at the University of Massachusetts Amherst.

I would like to thank my research group, Michael Nguyen, Zehui Xia, Joann Rodriguez, and Leigh Hamlet for all the help and advice given to me during my time as a graduate student.

I want to give thanks to all the Faculty members and staff in the Civil and Environmental Engineering Department for their commitment to teaching me valuable lessons and for preparing me for the field in which they all have greatly excelled in.

Finally, I would like to thank my fellow graduate students, my friends, and my family for the constant support and good times during my academic years.

Effects of Sulfidation on the Deposition and Detachment of
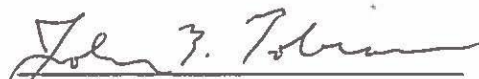
Silver Nanoparticles

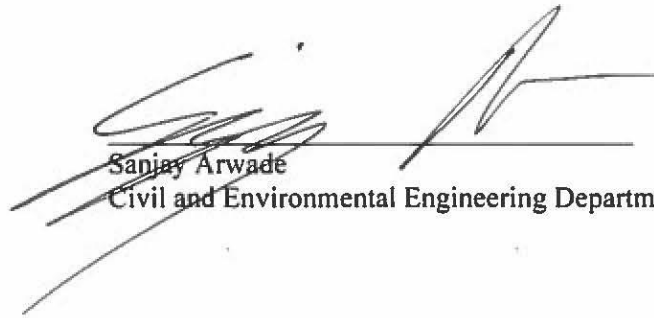A Masters Project Presented

by

Joseph Murphy

Approved as to style and content by:

_____
Boris Lau, Chairperson

_____
John E. Tobiason, Member

_____
Sanjay Arwade
Civil and Environmental Engineering Department

Abstract

The transformation of silver nanoparticles (AgNPs) due to environmental factors can play a role in their fate and transport in aquatic systems. Sulfidation has the potential to alter these particles' physio-chemical properties and their subsequent mobilization in aquatic environments. The water chemistry (e.g. pH, dissolved organic carbon) of these systems can also change the behavior of AgNPs. To better understand the effects of sulfidation on the characteristics and deposition of AgNPs, techniques such as quartz crystal microgravimetry (QCM) and dynamic light scattering (DLS) were used. In this study, AgNPs with two different ligand types, Polyvinylpyrrolidone (PVP)-capped AgNPs (PVP-AgNPs) and Polyethylene glycol (PEG)-capped AgNPs (PEG-AgNPs), were modified through sulfidation in the presence of natural organic matter (NOM). Sulfidation of PVP-AgNPs resulted in a 5 to 23 times greater extent of deposition to a silica substrate than unmodified PVP-AgNPs in tested conditions. This probably caused by the loss of steric repulsion due to the loss of PVP ligand during sulfidation. The dependence of ligand type on the effects of sulfidation were observed in the same conditions with sulfidized PEG-AgNPs having a 28%-98% decrease in deposition extent compared to pristine PEG-AgNPs. This decrease in particle-substrate interaction is attributed to the increase in electrostatic repulsion. Rates of deposition of each particle type were also reported to better understand the potential of these AgNPs to persist in engineered and natural aquatic environments. Hydrophobicity of AgNP types were not found to play a dominant role in the deposition dynamics. AgNP deposition extent to silica substrate provides insight on the potential for persistence in aquatic environments as well as a predisposition towards removal through media filtration. Based on deposition results, after sulfidation, PEG-AgNPs are more likely to persist than that of PVP-AgNPs.

Table of Contents

List of Figures and Tables

1.0 Introduction

1.1 Relevance and Significance of AgNPs

The emerging use and incorporation of silver nanoparticles (AgNPs) in commercial [1,2] and medical products has grown to make up nearly 25% of all nanomaterials on the consumer market largely due to their antimicrobial characteristics.[3] Silver (Ag) containing nanoparticles are the fastest growing group of nanomaterials in the present market.[2] Because of their rapid use in consumer products, their emergence in aquatic systems is of increasing concern.[4] Benn and Westerhoff [5] reported that because more than 70% of the U.S population is served by public sewers, the washing of clothes containing AgNPs would release silver that would arrive at a wastewater treatment plant (WWTP) where the AgNPs can potentially partition onto biomass and find its way into the environment through agricultural applications of treated bio-solids.

1.2 Design and Functionalization of AgNPs

The most common method of synthesizing AgNPs comes from the utilization of silver nitrate as the source of Ag^+ ions and the use of a reducing agent, such as citrate and ascorbate,[6] to control the precipitation and agglomeration of the particles. [6,7] The synthesis and functionalization of AgNPs is dependent on their intended application. Controlling shape and size during design of these particles plays a role in their characteristics[8] such as their optical (decrease in band gap with decrease in size[9]), and catalytic (increase hydrogenation with decreased size[10]) properties.

In order to control shape and modify the functionalization of these AgNPs, the use of various capping agents to passivate the NP surface is crucial for its function. The adsorption of polymer

on the AgNP surface to achieve stabilization has also been incorporated into synthesis

methods.[7,11] The addition of a polymer ligand to a solution of NPs will lead to stability as well as

an enhancement of its properties (e.g. size, shape).[11] Since characteristics such as size and

capping type for AgNPs are constantly being modified, it is important to understand their

behaviors in the environment. Polymers such as polyvinylpyrrolidone (PVP) are widely used for

particle stabilization due to its non-toxicity, solubility across many solvents, and inert

physiochemical properties.[12] A PVP molecule contains a hydrophilic moiety and a hydrophobic

alkyl group that make it desirable for NP stabilization.[12] Similarly, polyethylene glycol (PEG) has

been used extensively as it is non-toxic, water soluble, and can increase cell uptake in drug

delivery for certain systems of the human body.[13]

1.3 Environmental Behavior of AgNPs

Due to the increasing applications of AgNPs, there has been considerable research effort in

recent years on their speciation in natural aquatic[14, 15] and engineered aquatic systems.[1,16]

Characteristics of the particles after synthesis will play a role on the behavior of AgNPs. In 2013,

Agnihotri et al.[17] reported that AgNPs less than 10 nm in diameter show a strong increase in

antibacterial efficacy. Similarly, the synthesis of silver-polystyrene core-shell NPs have been

prepared for the use of antimicrobial characteristics.[7] AgNPs have the potential to be transformed

in the aqueous environment.[18-20] Transformation of AgNPs in the environment will depend on the

specific process as well as the characteristics and properties, such as ligand type,[21] of the AgNPs.

2

1.3.1 Photo Reduction

Ultraviolet radiation from the sun can transform and alter the fate of the NPs.[14, 21] Ligand and core type also play a significant role on the extent of these affects as well as their behaviors. In 2011 Li, et al.[22] demonstrated that light irradiation can enhance the release of silver ions (Ag^+) (14% increase) from photoactive citrate-capped AgNPs due to photo reduction of citrate and photo-induced morphological changes. It was also found that citrate-capped AgNPs aggregated (about double the diameter after 1 day) in the presence of light, potentially from photo induced fragmentation and fusion of the NPs. Phototransformation of PEG functionalized gold NPs has been reported to be more susceptible to aggregation due to the fragmentation of polymer on the NP surface.[19] It was found that PVP-capped AgNPs (19.9 nm average diameter) exhibited a slower rate (18% decrease) of dissolution compared to citrate capped-AgNPs (16.6 nm average diameter) after UV exposure for 5 hours that may occur in an aquatic environment or during wastewater treatment.[21]

1.3.2 Dissolution

Once AgNPs enters an aqueous environment, release of Ag^+ due to the dissolution of AgNPs can occur and result in a potential toxicity concern.[23] Many environmental factors will play a role in the release of dissolved silver. An increase of pH from 4 to 9 has been shown to decrease dissolution by 83%. A decrease in dissolved oxygen concentrations and the addition of natural organic matter have also been reported to decrease the extent of release of silver ions from AgNPs[24]

1.3.3 Sorption of Environmental Organics

In many freshwater systems, AgNPs bind with organic macromolecules[25-27] and decrease AgNP toxicity to aquatic organisms.[27] In 2015, Yin et al.[28] suggested that the pH, molecular weight of the natural organic matter, and the ligand type of the NP play a direct role in their adsorption to the AgNP surface. Enhanced steric stabilization has been reported due to the presence of dissolved organic carbon (DOC).[29]

1.3.4 Sulfidation

The interactions of AgNPs with reactive sulfur species can alter their fate and transport in aquatic environments. When released from consumer products, AgNPs will transport through sewer systems and wastewater treatment plants (WWTPs) where anaerobic conditions exist and the presence of hydrogen sulfide will promote the generation of Ag_2S.[16] Acid volatile sulfide (AVS) concentrations within a sewer system have been found to range from 120 to 150 mM.[30] The sulfidation of AgNPs will alter their behavior once they are discharged to an aquatic environment. In 2013, Kaegi et. al [30], showed that ~15% of PVP capped AgNPs became sulfidized within 5 hours of reaction with raw wastewater. Kaegi et. al [31] also reported that >90% of AgNPs were partially transformed into Ag_2S 2 hours after being spiked into a sample of mixed liquor from a non-aerated tank in a WWTP.[31] It is also suggested that sulfidation is size dependent where after 24 hours 100% of 10 nm AgNPs were sulfidized compared to 10% sulfidation of 100 nm AgNPs, this difference dictates NP behavior after discharge into an aquatic environment.[30] Furthermore, it has been reported that an increase in the sulfidation rate occurred at a size difference of 30 nm to 5 nm for citrate-stabilized AgNPs. Understanding the effects of

sulfidation on AgNP characteristics is vital in order to assess their fate and transport in the environment. [32]

1.3.5 Aggregation

Aggregation of particles has been studied extensively for many years. The most common theory to explain the interactions between particles and their rate of aggregation is the Derjaguin Landau Verwey Overbeak (DLVO) Theory.[33,34] It has been used to study particle-particle interactions (homoaggregation) and particle attachment to unalike particles (heteroaggregation). DLVO theory incorporates the overall sum of the van der Waals attractive forces and the electric double layer (EDL) forces (usually repulsive) to predict the aggregation or attachment of similar particles.[35]The solution chemistry as well as the particle surface effects the EDL repulsion between particles.[35]For example, an increase of the ionic strength results in a compression of the EDL and therefore a decrease of the repulsive forces. Similarly, a decrease in ionic strength causes an increase in EDL force and therefore induces a stronger repulsion.[36] A decrease in the ionic strength can in turn reverse the deposition of AgNPs to a collector surface such as silica when the extent of the EDL forces is increased.[37]

Environmental factors such as interactions with NOM have been shown to inhibit aggregation of AgNPs with various cappings.[28, 30] Depending on the ligand type, aggregation of AgNPs can occur due to photoinduced fusion and fragmentation of the NPs.[19, 38]

1.4 Research Objectives

The purposes of this study are 1) to determine the impact of sulfidation on the deposition and detachment dynamics of AgNPs and 2) to understand how these dynamics will differ in various water chemistries (e.g. pH, NOM) by characterizing the physicochemical properties (e.g. size, zeta potential, and hydrophobicity) of the NPs. A decrease in ionic strength was used to examine the reversibility of AgNP deposition. Previous studies have shown the effects of sulfidation and NOM interactions on the transformation and deposition of AgNPs.[39] Very little is known about the extent to which the detachment of these particles occurs after deposition. Alterations of NP properties can also be different in various environmental settings. Factors such as pH and dissolved organic carbon (DOC) were examined to better understand the role of solution chemistry in the deposition and detachment of AgNPs.

Quartz crystal microgravimetry (QCM) was used to determine the deposition and detachment kinetics of AgNPs (before and after sulfidation) onto a silica substrate. Furthermore, dynamic light scattering (DLS) was used to measure the size and charge of each type of AgNPs to determine which properties of the AgNP play a role in its deposition and detachment kinetics.

2.0 Methods

2.1 Preparation of AgNP suspensions

PVP and PEG-coated AgNPs were purchased from NanoComposix (San Diego, CA). Both core diameters were reported to be 50 nm by the manufacturer based on transmission electron microscopy (TEM). The molecular weight of the PVP and PEG used in the synthesis were 40 kDa and 5 kDa respectively. All particle suspensions (1.24×10^{10} particles mL^{-1}), samples, and

stock solutions were prepared using Milli-Q (18.2 mΩ) water using a Millipore system (Millipore). Particle background solutions were prepared in an electrolyte concentration of 50 mM $NaNO_3$ and 1 mM of buffer (HEPES, phosphate, and sodium bicarbonate for pH 5, 7, and 9 respectively), pH was adjusted with 100 mM HCl and 100 mM NaOH to achieve a pH of 5.0 ± 0.2, 7.0 ± 0.2, 9.0 ± 0.2 for each pH condition. Background solutions without the presence of particles were prepared for the phases of rinsing and desorption for testing with QCM. All background solution was filtered with a 0.2μm filter before use.

Unfractionated Suwanee River NOM (SRNOM) was purchased from the International Humic Substance Society (International Humic Substances Soc. MN). Stock solution of NOM (200 mg L^{-1}) was prepared in Milli-Q water and sonicated to insure homogenous mixture. NOM stock solution was stored in the dark at 4°C. NOM was added to NP suspensions to give an overall concentration of 5 mg L^{-1} as C.

2.2 Sulfidation

AgNPs were sulfidized in the presence of NOM. The sulfidation procedures described by Levard et al (2011)[40] were used to study the potential transformation of the NPs in a wastewater treatment system. Particles were mixed with sodium sulfide (Na_2S) in the presence of 40 mg L^{-1} NOM with a S/Ag ratio of 1.079. The solutions were mixed for 24 hours in the dark before being centrifuged at 5000 rpm for 25 minutes two times to ensure the removal of excess Na_2S and NOM that had not been bound to the AgNP surface. Pellets formed by centrifugation were then suspended in relevant conditions to study different environmental factors as described. This procedure was performed on both PVP-capped and PEG-capped AgNPs. Solutions were purged

with nitrogen gas before being suspended.

Four nanoparticle types were analyzed in this study: (1,2). PVP-capped and PEG-capped AgNPs that received no used as received (PVP-AgNPs, PEG-AgNPs) and (3,4) PVP-capped and PEG-capped AgNPs that underwent sulfidation in the presence of NOM (Sulf-PVP-AgNPs, Sulf-PEG-AgNPs). Each AgNP type was measured in three different pHs (5, 7, and 9) and in the presence of/without 5 mg-C L^{-1} NOM.

2.3 QCM

2.3.1 Deposition and Detachment Extents of AgNP.

Deposition and desorption extents were quantified for each type of AgNPs in various solution chemistry conditions by QCM (Q-Sense AB, Gothenburg, Sweden) at 25°C. Frequency shifts of an oscillating quartz crystal (Δf) occur when mass is being deposited onto the sensor surface (Δm). The relationship between Δf and Δm is described by the Sauerbrey relation[42]:

$$\Delta m = C \, \Delta f \, n^{-1}$$

Where C is the sensitivity constant for the quartz crystal (17.7 ng cm^2 Hz^{-1}) and n is the overtone of which Δf is evaluated.

In this study, silica-coated quartz crystal sensors (QSX 303, Q-Sense AB, Gothenburg, Sweden) were used as the substrate surface for the deposition of AgNPs. Sensors were cleaned by soaking

in sodium dodecyl sulfate (SDS) over extended periods of time, rinsed with ultrapure water, dried with N_2 gas and then cleaned in a UV/Ozone cleaner (UV/Ozone Pro Cleaner) for 30 min to remove any contaminants or trace organics before each experiment.

Sensors were placed in flow-through modules and all solutions were well mixed and injected at a constant flow of 0.1 mL min^{-1}. Background solution (50mM NaNO$_3$) without the particles were passed through for 25 min to achieve a baseline ($\Delta f < 0.1$ Hz min^{-1}). Well-mixed AgNP suspensions with the same solution chemistry as the background solution were then allowed to pass through the sensor module and real time deposition was recorded. The background solution used for to establish a baseline was then being used again as a rinsing buffer for 15 minutes before a new buffer with lower ionic strength (5mM NaNO$_3$) was injected to induce detachment of particles from the silica substrates. The extent of mass deposition as well as detachment for each type of AgNPs were determined using the Sauerbrey relation. The third overtone of the Δf was used as it had the best signal-to-noise ratio. Triplicate measurements were performed.

2.3.2 Rates of AgNP Deposition.

Deposition rates for each different type of AgNPs were measured as well using QCM. Hughes et al.[37] developed a QCM-based method to generate sorption isotherms using the Δf recorded at varying AgNP concentrations. When an ultimate frequency was achieved, the measured kinetics was fit by an equation relating to a Langmuir isotherm adsorption [43, 44]:

$$\Delta f(t - t_0) = \Delta f(\infty)[1 - \exp(-k_{obs}(t - t_0))]$$

Where $\Delta f(\infty)$ the maximum frequency shift for monolayer adsorption, k_{obs} is the observed rate of the frequency shift by the real-time QCM measurements, and $t - t_0$ added to eliminate the mixing affect of the solution before it reaches the sensor. The data was then fit by a non-linear regression using a Gauss-Newton algorithm. Isotherm rates k_{obs} were calculated. The k_{obs} for varying concentrations can then be described by the equation

$$k_{obs} = Ck_a + k_b$$

Where C is concentration and k_a and k_b are the adsorption and desorption rates respectively. Finding values for k_a can used to compare the rate of each different particle type to better understand the attachment kinetics. All runs were performed in 50 mM NaNO$_3$ at pH 5.0 ± 0.2.

2.4 Characterization of AgNPs

2.4.1 Size and Zeta Potential.

The average hydrodynamic diameter (AHD) as well as the electrophoretic mobility of AgNPs were measured using a Malvern Zetasizer NS (Worcestershire, U.K.). The zeta potential (ZP) was estimated from electrophoretic mobility using the Smoluchowski approximation. All measurements were performed at 25°C.

2.4.2 Relative Hydrophobicity

Procedure for hydrophobicity measurements was adapted from Xiao & Wiesner.[45] Rose Bengal (RB) dye was purchased from Alfa Aesar. RB dye has been shown to increase their adsorption to

particle surfaces with greater hydrophobicity and has been used as a probe molecule for the

measurement of hydrophobicity of particles related to drug delivery in pharmaceutical studies.[46-48] Briefly, 20 mg L^{-1} of RB dye was added to different suspensions of AgNP of increasing

concentration in 1.5mL centrifuge tube in background solution with 1mM phosphate buffer at pH

7.0 ± 0.2. Solutions were mixed for 3 h in the dark at 25°C. Particles were then centrifuged at

15000 rcf for 1hr. and 15 min. The supernatant was collected and absorbance was recorded at a

wavelength of λ=549nm using a Biotek EL800x Plate Reader (Winooski, Vt., U.S.A.). The

partitioning quotient (PQ) was calculated by the following equation:

$$PQ = \frac{Mass\ of\ RB\ Dye\ absorbed\ on\ surface\ of\ NPs}{Mass\ of\ RB\ in\ solution}$$

The total surface area of the AgNP suspension was also calculated by assuming the suspension

were monodisperse and the particles were spherical and had a diameter equal to the

hydrodynamic diameter provided by DLS measurements. Plotting the PQ against the Total

surface areas gave straight lines where linear regression fits gave slopes that were used to

compare the hydrophobicity of each type of AgNPs in a relative manner. Triplicates of

measurements were performed.

2.4.3 Relative Contribution of Steric Forces on the stability of AgNPs.

Steric forces between NPs due to polymer-polymer repulsive interaction will play a role in the

stabilization of NP suspensions. In a "good" solvent such as water, we expect to see full polymer

chains that extend and induce steric interactions between NPs. In a "poor" solvent like acetone,

the polymer ligand will coil and steric repulsion will be reduced and destabilization will potentially occur.

In order to evaluate the contribution of steric forces in the stabilization of the different AgNP types, particles were suspended in solvents varying in ratios of acetone to water (from 1:2 acetone: water to 3:1 acetone: water) in 50mM $NaNO_3$ at pH 7 with phosphate buffer . Six particle types were evaluated: (1,2). PVP-capped and PEG-capped AgNPs used as received (3,4) PVP-capped and PEG-capped AgNPs that underwent sulfidation in the presence of NOM (5,6) PVP-capped and PEG-capped AgNPs that underwent sulfidation without the precense of NOM. Time-resolved DLS were performed for respective particle suspensions to evaluate the change in AHD over time.

3.0 Results and Discussion

3.1 Deposition Extent and Rates

3.1.1 Effects of Sulfidation

The extent of deposited mass (ng cm^{-2}) for each particle type onto the silica substrate was reported for various conditions (Apdx.1). Sulfidation of PVP-AgNPs resulted in higher extent of deposition onto the silica substrate (Fig.1). A 5 to 23 times increase was observed in the extent of PVP-AgNP deposition after sulfidation for the tested pH and DOC conditions. It has been reported that a loss of PVP ligand occurs as a result of sulfidation of AgNPs.[49] This loss of capping can result in a decrease of the steric repulsion and therefore increase the extent of

deposition. The steric repulsion induced by the already deposited PVP-AgNP can also hinder further particle deposition through steric hindrance.

In contrast, sulfidation of PEG-AgNPs resulted in a decrease of deposition extent at pH 5 (28%-81% decrease) and 7 (91%-98% decrease) regardless of background NOM concentration in solution (Fig. 2). The PEG-AgNPs may have been sulfidized to a larger degree than the PVP-AgNP due to the molecular weight size difference of the two ligands. Since the PEG ligand is 8 times smaller than PVP (5kDa vs. 40kDa), sulfide ions may have a faster penetration through the ligands to react with the core surface of the AgNPs. Sulfidized PEG-AgNPs always possessed a more negative charge than pristine PEG-AgNPs (Fig. 3). This could be due to the formation of Ag_2S on the particle surface. Therefore, a decreased deposition extent of Sulf-PEG-AgNPs could possibly due to stronger electrostatic repulsion induced by the more negatively charged particle surface. In contrast, ZP of PVP-AgNPs became less negative after sulfidation (except pH 7, 5 mg-C L^{-1}) (Fig. 4).

Deposition rates for each particle type at pH 5 and 0 mg-C L^{-1} was determined (Table 1) using QCM with a range of particle concentrations. Sulfidation of both PVP-AgNPs and PEG-AgNPs decreased the rate of deposition (roughly 20 times slower for PVP and 71 times slower for PEG).

The hydrophobicity of each type of AgNPs were compared using the slopes of the linear regressions shown in Figure 5. While PEG-AgNPs became more hydrophobic after sulfidation, PVP-AgNPs became more hydrophilic after sulfidation. The hydrophobicity of Sulf-PVP-AgNPs and Sulf-PEG-AgNPs are very similar in hydrophobicity (slopes = 0.3198 and 0.3135). If

sulfidation made the particles more hydrophilic, a reduction in the deposition extent is anticipated as the particles will have a higher affinity towards the bulk solution as opposed to the silica substrate. However, the opposite was observed in this study. Therefore, hydrophobicity does not seem to play a dominant role in controlling the deposition of AgNPs.

3.1.2 Effects of Water Chemistry

The extent of deposition for all particle types at various pHs are shown in Appendix 1. The pH affected the extent of deposition for certain particle types. For example, the extent of Sulf-PVP AgNP deposition (Fig.7) decreased nearly 23% (4845.5 ng cm^{-2} to 3732 ng cm^{-2}) from pH 5 to pH 7. No detectable deposition was observed at pH 9 in the absence of NOM. The minimal deposition at pH 9 may have been due to a stronger electrostatic repulsion between the Sulf-PVP-AgNPs and the silica substrate with an increase in pH.

The extent of PEG-AgNP deposition (Fig. 8) also decreased roughly 68% from pH 5 to 7 and no deposition at pH 9 in the absence of NOM. As the pH shifted 5 to 9, silica became more negatively charged with the hydroxylation of the substrate. The extent of PVP-AgNP deposition remained consistent (average of all extents being no more than 23% away from minimum or maximum deposition) in all pHs. As seen in Appendix 3, the ZP of the PVP-AgNPs in most pH conditions did not vary greatly. Sterically stabilized PVP is an uncharged polymer that does not protonate or deprotonate as a function of pH. Therefore a significant change in zeta or size due to pH is not anticipated.[50] This means electrostatic interactions probably does not play a role in the deposition extent. The surface charge of PVP-AgNP which may alter the deposition extent is not affected by the pH change and may be due to the deposition being controlled by hydrogen

bonding between the carbonyl group in PVP and the hydrogen in the silanol group of the silica substrate.[51]

In the presence of NOM, Sulf-PVP-AgNPs had a decrease in deposition extent (Fig. 11) (43% and 55% for pH 5 and 7 respectively). NOM macromolecules may adsorb to the surface of the AgNPs during sulfidation. The adsorbed NOM together with the unbound NOM seems may have increased electrosteric repulsion to decrease particle-substrate interactions.[29]

3.1.3 Effects on Steric Stabilization

Results on the contribution of steric forces in different poor and good solvent ratios can be seen in Figure 6. PVP-AgNPs began to destabilize in the strongest ratio (3:1 acetone:water) to roughly 500 nm. Since it took the highest concentration of poor solvent to reduce the steric forces between ligands on each particle surface, then it is likely that steric stabilization is a strong contributor to the stabilization of these NPs. After sulfidation of PVP-AgNPs without the precense of NOM, we see particle aggregation in the 2:1 acetone:water ratio. This means there is a reduction in the steric repulsive forces and therefore it took a weaker concentration of poor solvent to see destabilization. This is likely due to the loss of PVP ligand during the sulfidation process as discussed before. For sulfidation of PVP-AgNPs in the presence of NOM, the particles do not destabilize until the highest concentration of poor solvent. Interactions with NOM and the NP surface may cause further steric stabilization due to the large organic macromolecules.

In the case of PEG-AgNPs, there is no size change across the poor solvent rations we see size change at a lower concentration of acetone for sulfidized particles in the presence of NOM and then no size change with sulfidation in the presence of NOM. The NOM can again be further stabilizing the particles after sulfidation.

After sulfidation, PEG-AgNPs begin to destabilize in the 2:1 acetone:water mixture.
In the presence of NOM, sulfidation does not reduce the steric forces. The same effect from the NOM on the PVP-AgNPs may be similar to that of the PEG-AgNP where further stabilization is induced by interactions with NOM macromolecules.

3.1.4 Effects of Ligand Type

When comparing the two pristine particle types, PEG had a higher extent (1-6 times greater) of deposition than that of PVP for many background conditions (Fig. 9). This is likely due to the steric repulsion caused by the two capping types. PVP having a larger molecular weight (40kDa) (Fig.10) possessed higher potential for steric stabilization as opposed to PEG (5kDa). If the particles are dispersed due to steric stabilization, it may inhibit particle deposition to the silica substrate. Therefore, a polymer with a longer chain such as PVP may inhibit particle deposition more than that of PEG. When comparing rates, PEG-AgNPs has a higher rate of adsorption than that of PVP.

The contribution of steric forces to particle stabilization for both ligand types was evaluated. As seen in Figure 6, the change in AHD over time for various solvent ratios were used to determine the reliance of steric stabilzaiton from polymer-polymer interactions for particle stability was

used for both PVP-AgNP and PEG-AgNP. From the results, it is seen that after 20 minutes, PVP-AgNP increased in AHD to 500 nm.

PEG-AgNPs are more hydrophilic than PVP-AgNPs (Fig. 5). PEG capping used in synthesis is 5 kDa compared to that of 40 kDa of the PVP capping. The size difference may explain the difference in particle hydrophobicity. Again, if PVP-AgNP is more hydrophobic, we expect to see a higher deposition extent in the hydrophobic particles having a higher affinity to partition out of the water phase and onto the substrate. Based on deposition results we see a higher extent of deposition for PEG-AgNP for most cases. Therefore, it seems that other forces play a dominant role in the deposition kinetics.

3.2 Detachment

A decrease in ionic strength (50mM to 5mM $NaNO_3$) will induce the detachment of particles to the silica substrate and the mass change is presented (Apdx. 4). According to DLVO theory, a decrease in the ionic strength of the solution will lead to a relaxation of the EDL and therefore increase the repulsive forces.[52]

Sulf-PVP-AgNPs had the most noticeable extent of detachment when comparing relative to other particle cases in all pH and NOM conditions. Without the presence of NOM, there was substantial detachment of Sulf-PVP-AgNP compared to other particle types (Fig.12). This may be because deposition of the Sulf-PVP-AgNP is dominated by electrostatic interactions.

For PVP-AgNP at pH 5 with 5 mg-C L^{-1} NOM, we see further deposition was observed during the induced detachment from the decrease in ionic strength (Fig.13). Since there are no AgNPs in

solution during the detachment phase, the further deposition is probably due to NOM in suspension. When comparing the case at pH 5 for PVP-AgNPs and 5 mg-C L^{-1} to the other pH conditions, this trend does not occur. This may be due to the active functional groups prevalent at pH 5 for the SRNOM that further inhibit deposition to either the silica substrate or the film of already deposited PVP-AgNPs.

The net deposition of each particle was determined by calculating the remaining deposited mass after the decrease in the ionic strength (Apdx.5). As shown, Sulf-PVP-AgNPs had the greatest mass deposition remaining after the increase of the EDL repulsive forces (Fig.14).

In terms of percent detachment (Apdx. 6) there were no noticeable differences between capping agents as well as pristine particles and their sulfidized counterparts. In no case did the average of any particle type in all conditions reach 100% detachment in the decrease in the ionic strength from 50mM NaNO$_3$ to 5mM, which gives reason to believe that there is attachment that is found in the primary minima in of the potential energy between the particles and substrate as suggested by DLVO.

4.0 Summary of Finding & Implications

Results from experiments relating to the characteristics as well as the deposition kinetics of PEG-AgNP and PVP-AgNP give a better understanding on the effects of sulfidation on the environmental implications of these engineered AgNPs. Depending on the ligand type, the sulfidation that can occur in a sewer system or WWTP can either enhance or diminish the persistence of AgNPs in aquatic environments.

The sulfidation of PVP-AgNPs can increase the deposition extent to a silica substrate compared to the as prepared pristine particle. This means in a filtration setting these particles will have a higher affinity to media such as sand. Similarly, in an aquatic environment, Sulf-PVP-AgNPs will more likely to partition out of solution and persist less in water compared to PVP-AgNPs. In contrast, the sulfidation of PEG-AgNPs can decrease its deposition extent to a silica substrate and therefore enhance the persistence of these particles in aquatic systems.

When looking at capping type, PVP-AgNP will deposit consistently throughout a range of pH. At pH 9, PEG-AgNP deposit to a smaller extent and therefore may persist longer in water. After the inevitable effects of sulfidation, PVP-AgNPs will be easier to be immobilized than PEG-AgNPs. Therefore, in synthesis of AgNPs, PVP as a polymer ligand over PEG can decrease the exposure of these particles in the environment and therefore might be a more environmentally benign polymer.

Water chemistry will also dictate the mobilization in which these AgNPs will persist. Generally, lower pH will induce higher deposition and a decrease in these particles persistence. Likewise, the presence of NOM will decrease the deposition extent and allow for further mobilization of these particles in water.

It is also important to determine the potential of detachment of these AgNPs from a silica substrate in order to understand its long-term fate and susceptibility to remobilization. Detachment extent overall was not affected by sulfidation for both particle types. Overall,

regardless of conditions, AgNPs that have already deposited will inevitably detach to a certain

degree. Therefore, it is important to further study not only the deposition kinetics, but also the

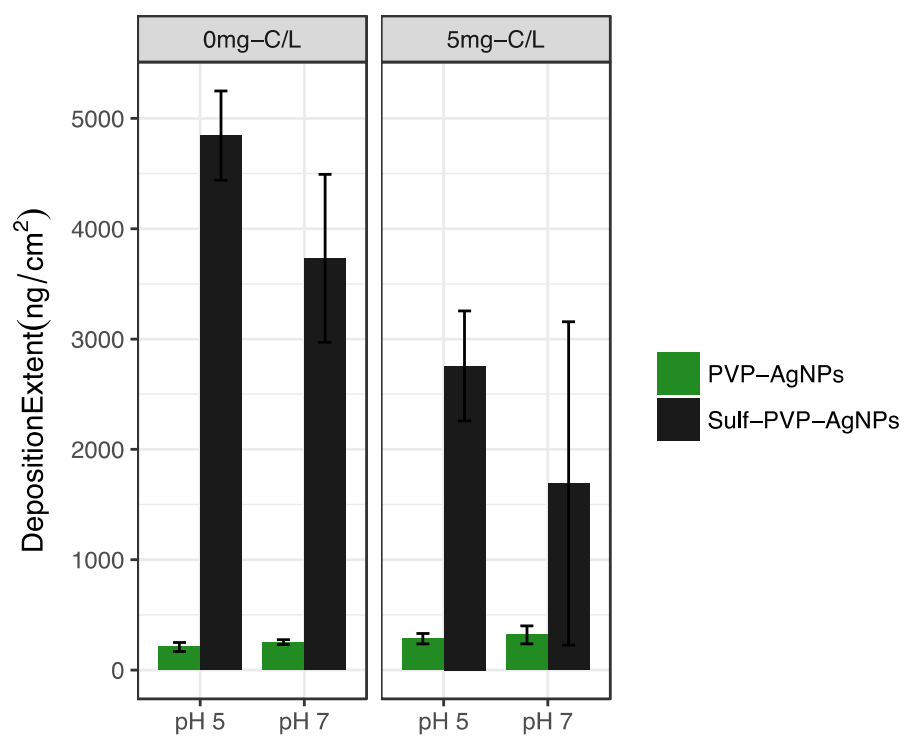potential for detachment and what factors may further induce it.

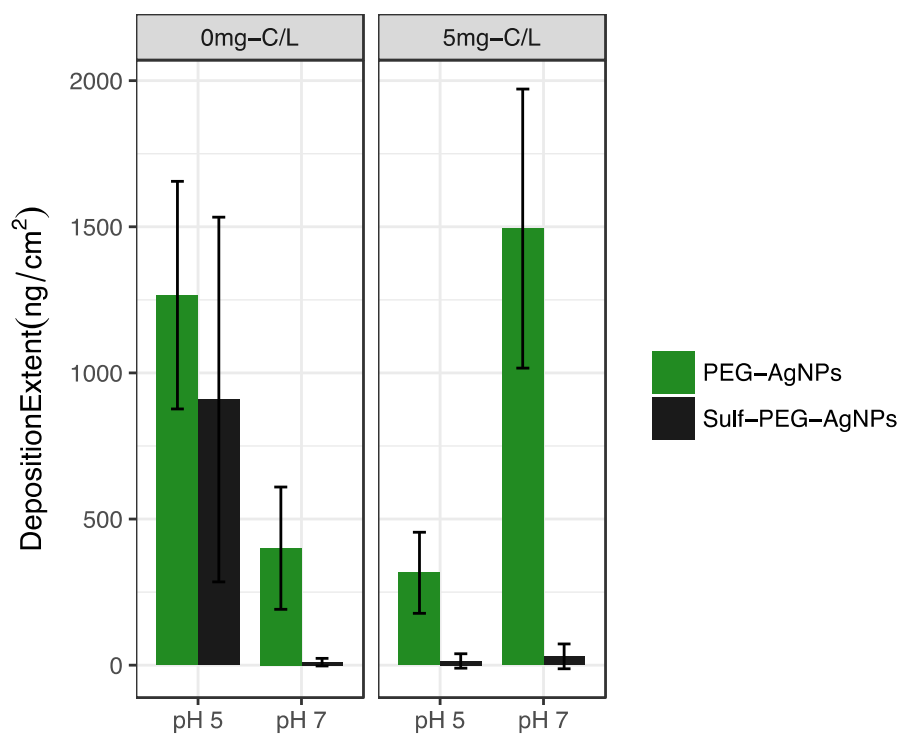**Figure 1.** Effects of sulfidation on the deposition extent of PVP-AgNPs.

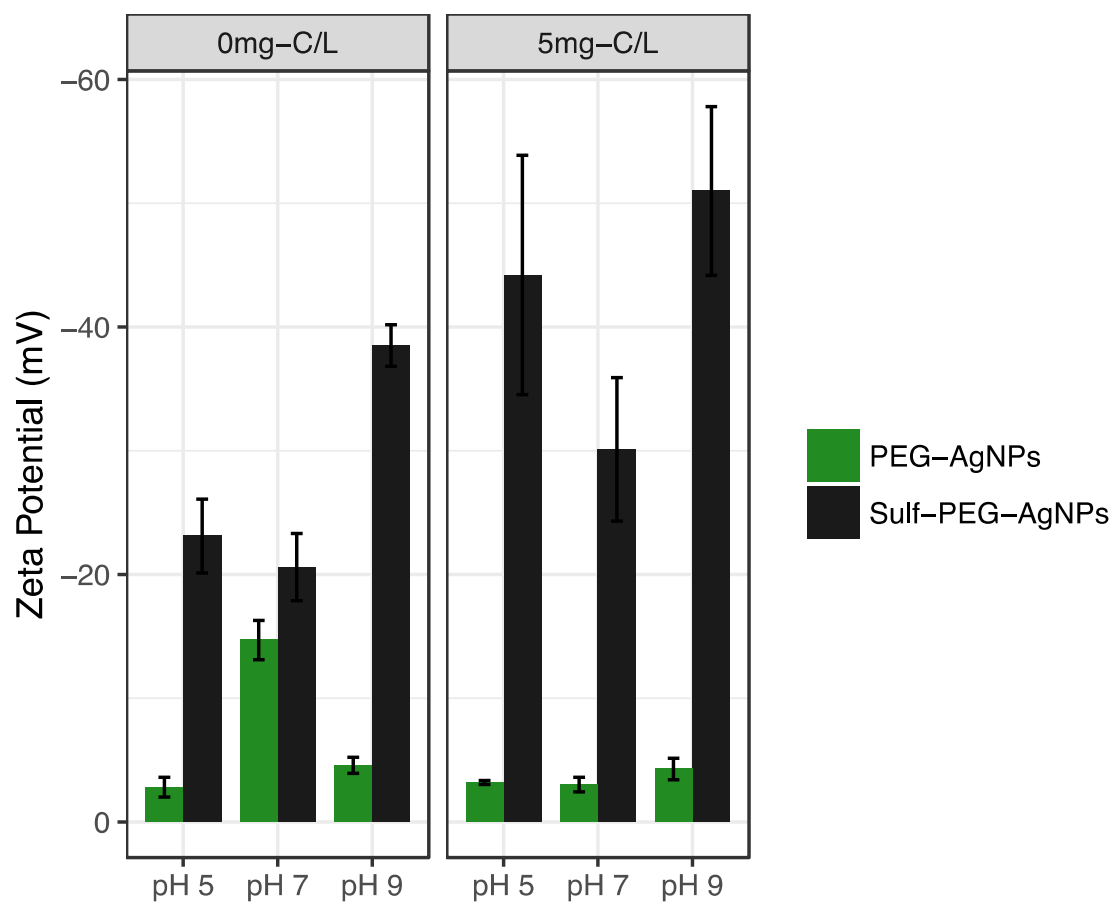**Figure 2.** Effects of sulfidation on the deposition extent of PEG-AgNPs.
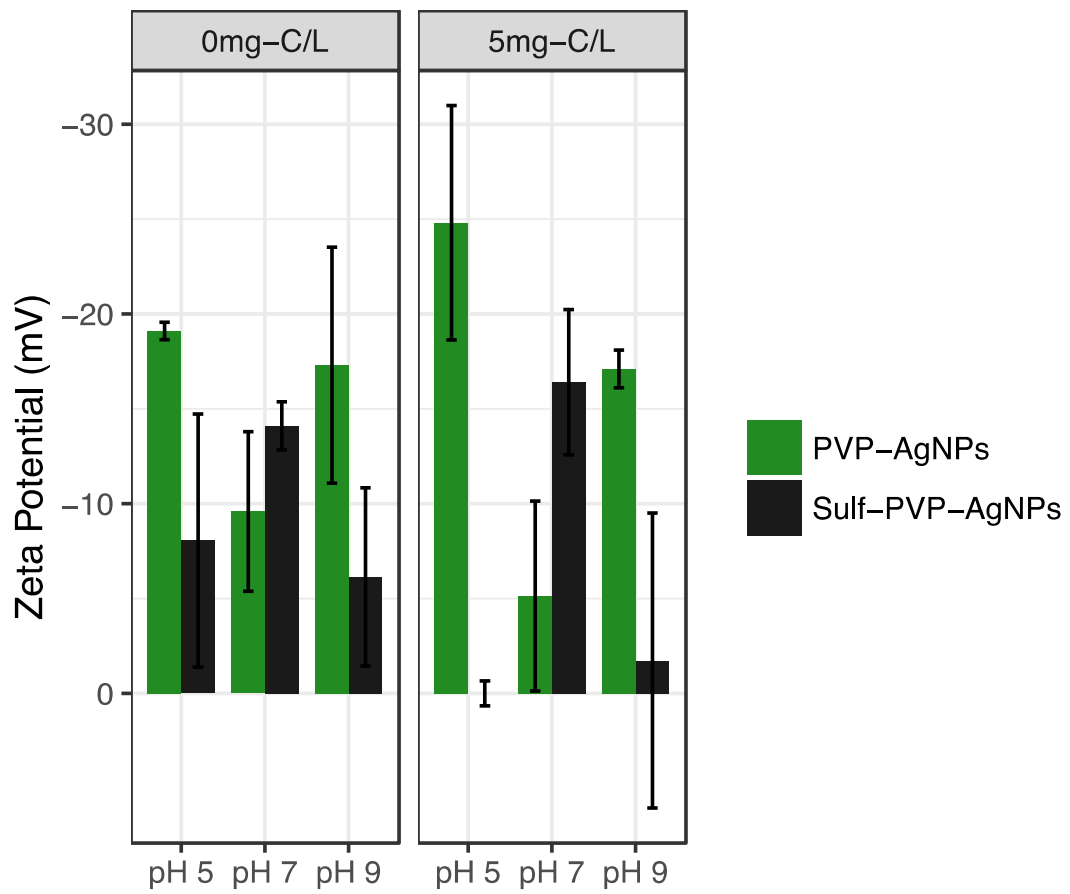
Figure 3. Zeta Potentials of PEG-AgNPs before and after sulfidation.

Figure 4. Zeta Potentials of PVP-AgNPs before and after sulfidation.
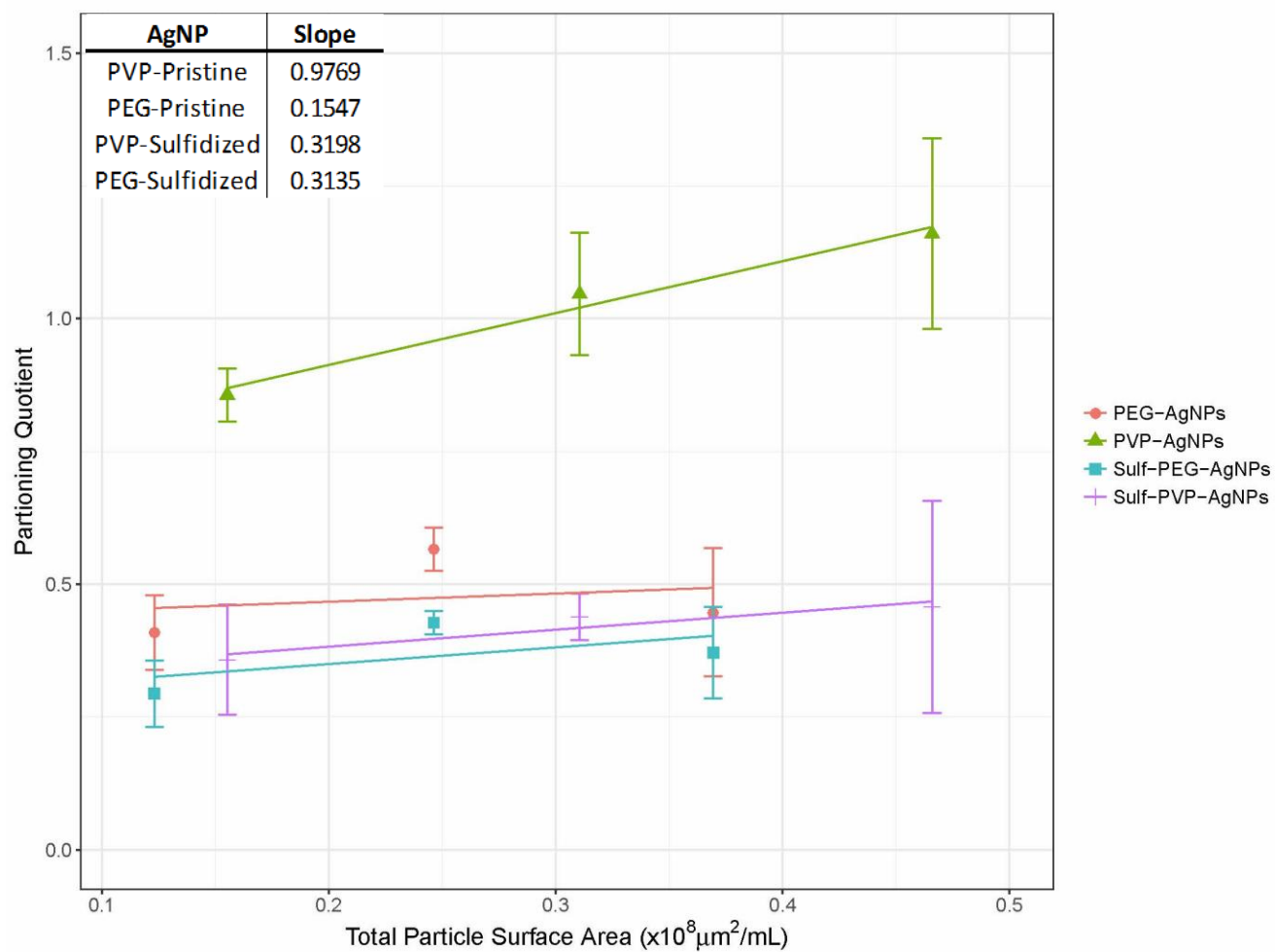
Figure 5. Relative hydrophobicity of AgNPs before and after sulfidation at pH 5.
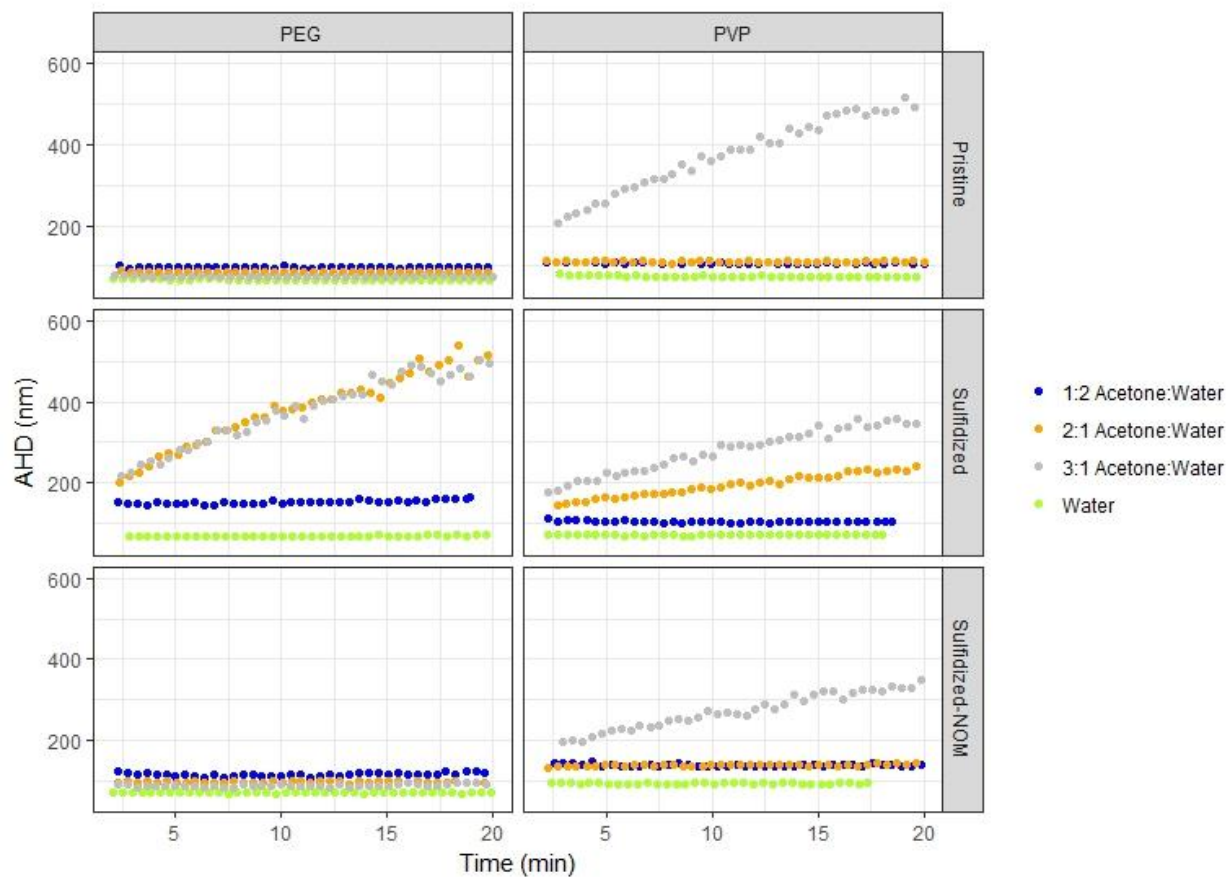
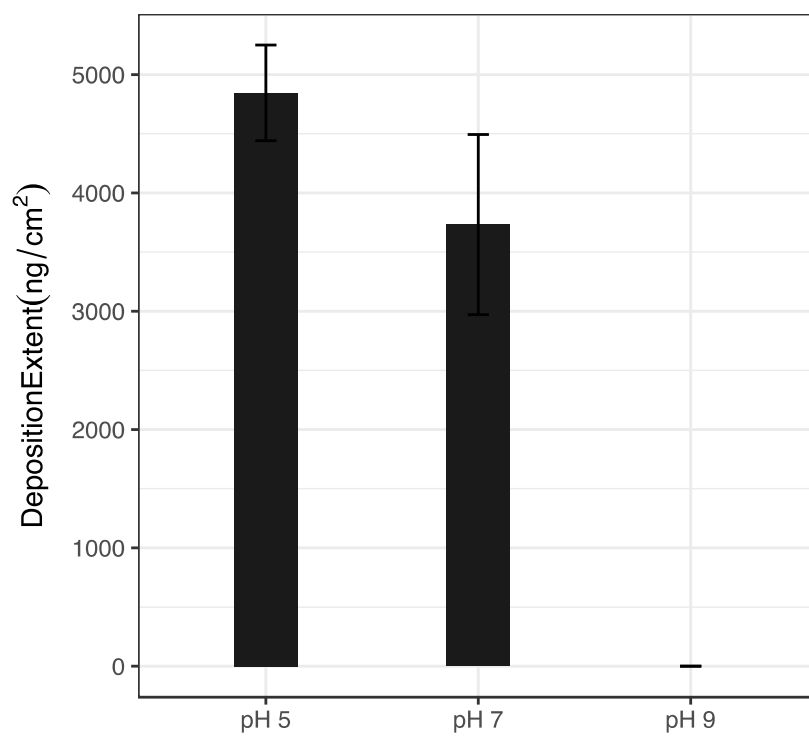**Figure 6.** Time-Resolved DLS Results for AgNPs in varying solvent ratios.
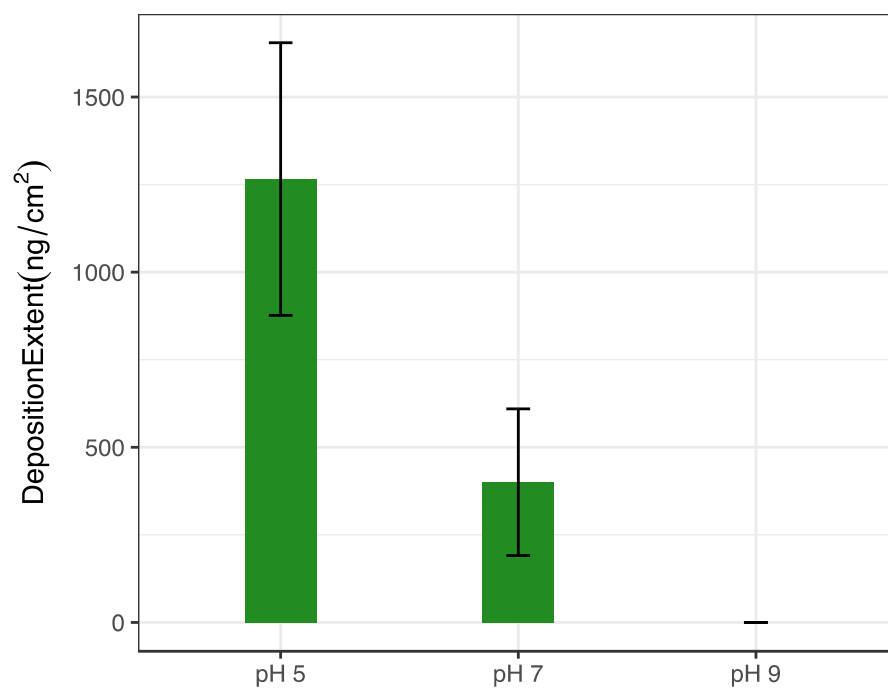
Figure 7. Effects of pH on sulfidized PVP-AgNPs.
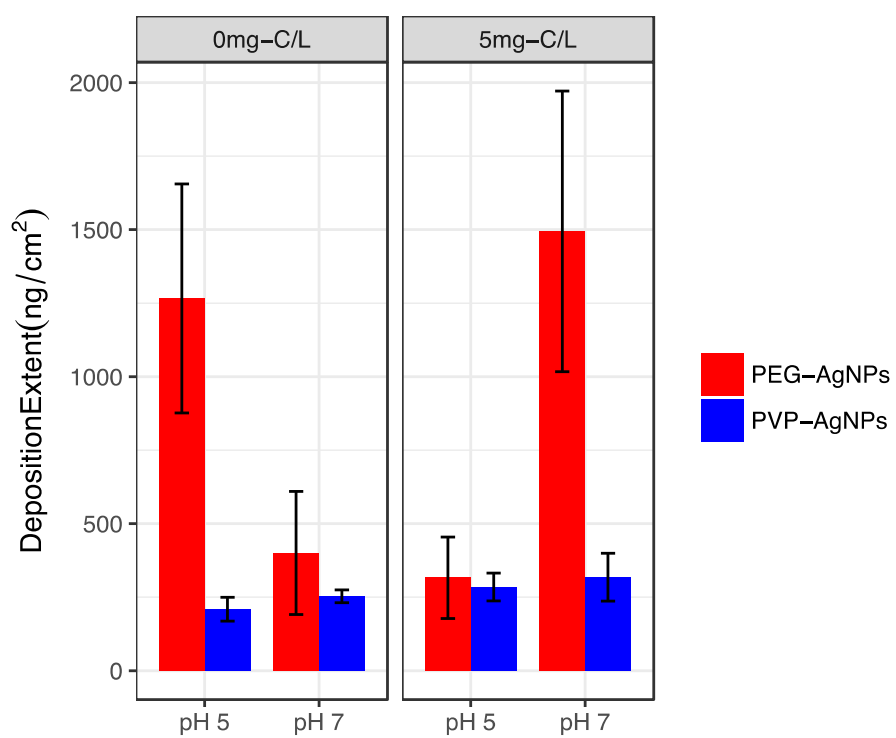
Figure 8. Effects of pH on PEG-AgNPs.

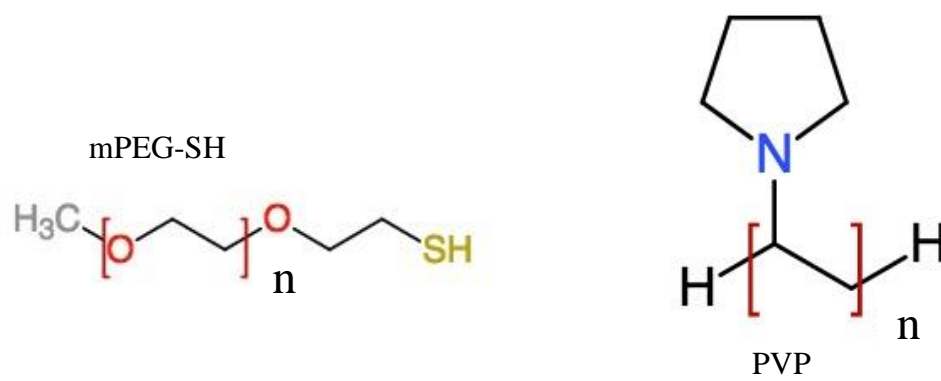**Figure 9.** Effects of ligand type on the deposition extent of AgNPs.

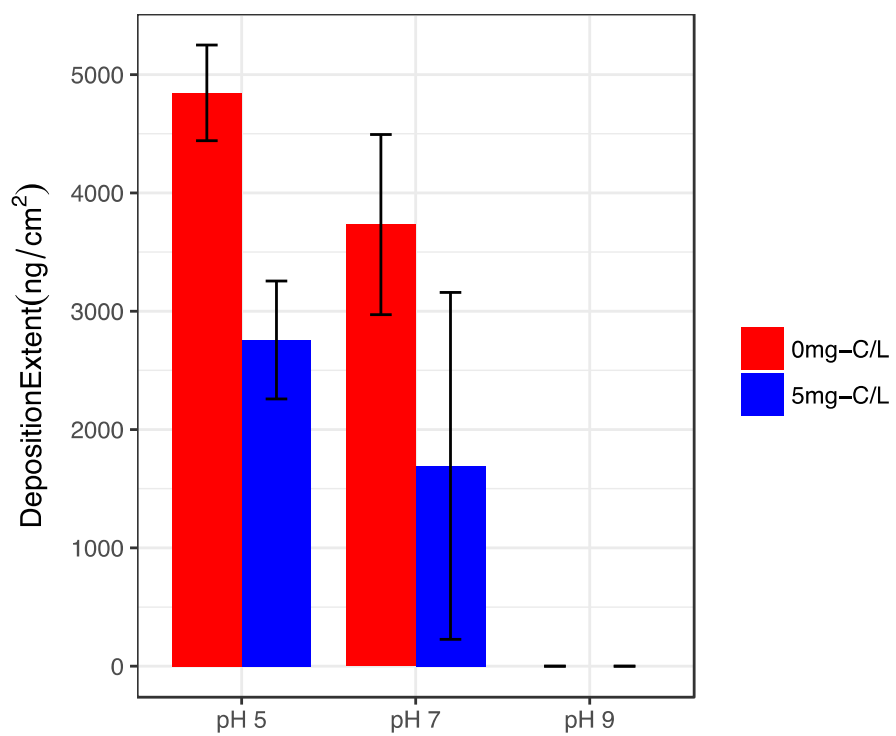**Figure 10.** Molecular Structure of mPEG-SH and PVP.

Figure 11. Effects of NOM on the deposition extent of sulfidized PVP-AgNPs.
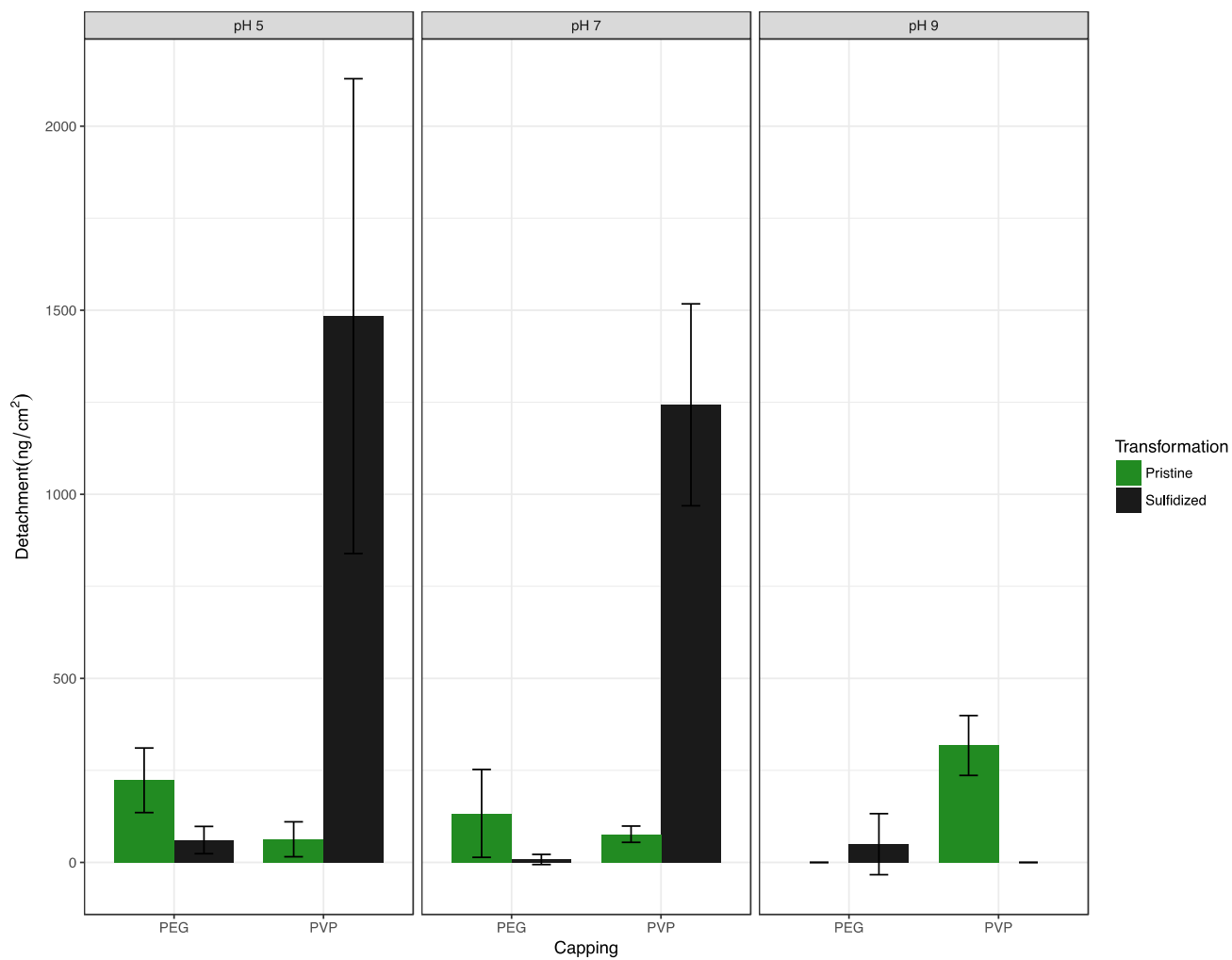
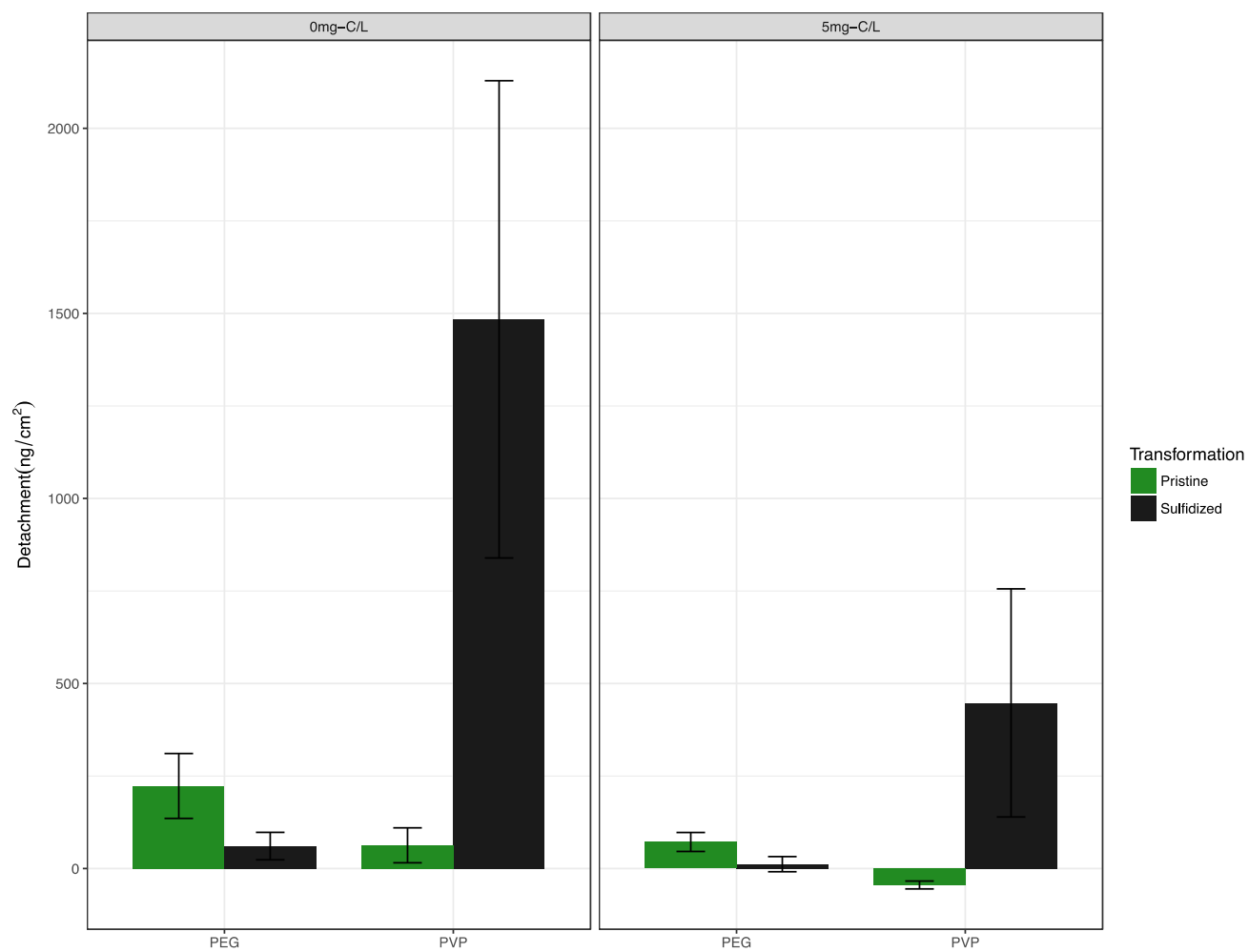**Figure 12.** Detachment extent of PVP-AgNPs and PEG-AgNPs before and after sulfidation.

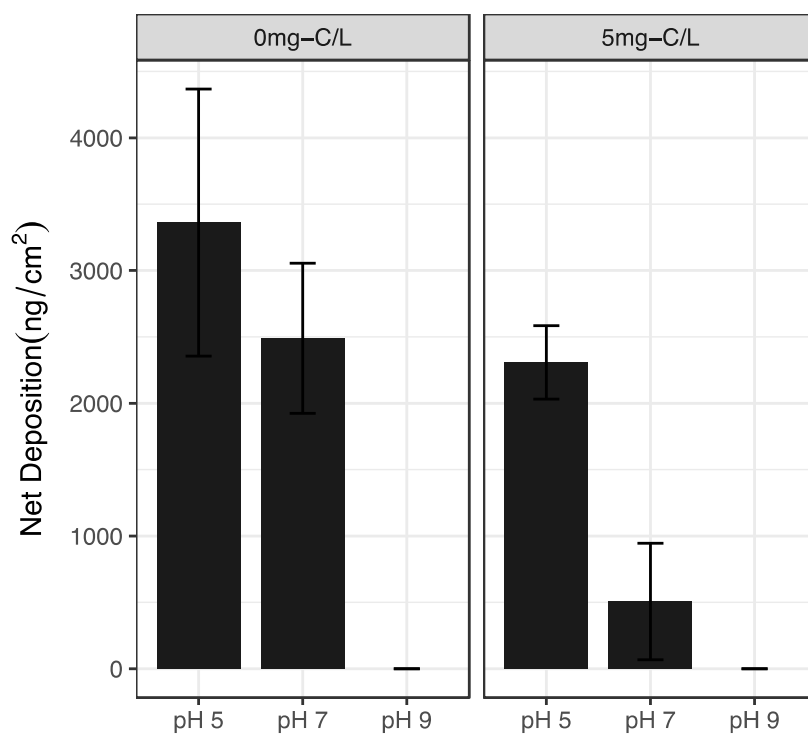**Figure 13.** Detachment extent of PVP-AgNPs before and after sulfidation.

Figure 14. Net deposition of Sulf-PVP-AgNPs.

Table 1. Observed rates (k_{obs}), Adsorption rates (k_a), and ultimate frequency shift ($-\Delta f(\infty)$) for all particle types. All measurements were performed at pH 5.

Particle Type	C (x 10^{10} particles mL^{-1})	k_{obs} (s^{-1})	$-\Delta f(\infty)$ (Hz)	k_a (x 10^{-13} mL particles^{-1} s^{-1})
PVP-AgNP	3.1	6.908E-04	58.63	0.10
	4.96	7.153E-04	67.36	
	6.2	1.158E-03	46.31	
PEG-AgNP	0.62	3.202E-03	20.45	5.00
	2.1	1.545E-02	21.26	
	4.96	2.590E-02	18.74	
PVP-Sulf-AgNP	1.24	8.590E-06	1671	0.005
	2.48	1.970E-05	3234	
	3.72	9.330E-05	3618	
PEG-Sulf-AgNP	0.62	3.462E-04	0.7737	0.07
	2.48	4.638E-04	5.022	
	3.72	5.659E-04	4.423	

References

1. Blaser, S. A., Scheringer, M., Macleod, M., & Hungerbühler, K. (2007). Estimation of cumulative aquatic exposure and risk due to silver: Contribution of nano-functionalized plastics and textiles. Science of the Total Environment 390.2–3 (2008): 396–409. Web. 21 Mar. 2017.

2. Fabrega, J., Luoma, S. N., Tyler, C. R., Galloway, T. S., & Lead, J. R. (2011). Silver nanoparticles: Behaviour and effects in the aquatic environment. *Environment International*, *37*(2), 517–531.

3. Chaloupka, Karla, Yogeshkumar Malam, and Alexander M. Seifalian. "Nanosilver as a New Generation of Nanoproduct in Biomedical Applications." *Trends in Biotechnology* 28.11 (2010): 580–588.

4. Benn, Troy et al. "The Release of Nanosilver from Consumer Products Used in the Home." Journal of environmental quality 39.6 (2010): 1875–1882.

5. Benn, Troy M., and Paul Westerhoff. "Nanoparticle Silver Released into Water from Commercially Available Sock Fabrics." Environmental Science and Technology 42.11 (2008): 4133–4139.

6. Abou El-Nour, Kholoud M M et al. "Synthesis and Applications of Silver Nanoparticles." Arabian Journal of Chemistry (2010): 135–140.

7. An, Jing et al. "Antimicrobial Active Silver Nanoparticles and Silver/polystyrene Core-Shell Nanoparticles Prepared in Room-Temperature Ionic Liquid." Materials Science and Engineering C 29.6 (2009): 1984–1989.

8. Sun, Yugang et al. "Shape-Controlled Synthesis of Gold and Silver Nanoparticles." Science (New York, N.Y.) 298.5601 (2002): 2176–9.

9. Lin, H. et al. "Size Dependency of Nanocrystalline TiO2 on Its Optical Property and Photocatalytic Reactivity Exemplified by 2-Chlorophenol." *Applied Catalysis B: Environmental* 68.1–2 (2006): 1–11.

10. Kart Kartusch, Christiane, and J A Bokhoven. "Hydrogenation over Gold Catalysts: The Interaction of Gold with Hydrogen." *Gold Bulletin* 42.4 (2009): 343–347.

11. Ehlert, Sascha et al. "Polymer Ligand Exchange to Control Stabilization and Compatibilization of Nanocrystals." *ACS Nano* 8.6 (2014): 6114–6122.

12. Ko Koczkur, Kallum M et al. "Polyvinylpyrrolidone (PVP) in Nanoparticle Synthesis." *Dalton Trans*. 44.October 2015 (2015): 17883–17905.

13. Jokerst, Jesse V et al. "Nanoparticle PEGylation for Imaging and Therapy." *Nanomedicine (London, England)* 6.4 (2011): 715–728.

14. Cheng, Y., Yin, L., Lin, S., Wiesner, M., Bernhardt, E., & Liu, J. (2011). Toxicity Reduction of Polymer-Stabilized Silver Nanoparticles by Sunlight. *J. Phys. Chem. C*, *115*, 4425–4432.

15. Mueller, N. C., & Nowack, B. (2008). Exposure Modeling of Engineered Nanoparticles in the Environment. *Environmental Science & Technology*, *42*(12), 4447–4453.

16. Kent, Ronald D., Joel G. Oser, and Peter J. Vikesland. "Controlled Evaluation of Silver Nanoparticle Sulfidation in a Full-Scale Wastewater Treatment Plant." Environmental Science & Technology 48.15 (2014): 8564–8572.

17. Agniho Agnihotri, Shekhar, Soumyo Mukherji, and Suparna Mukherji. "Size-Controlled Silver Nanoparticles Synthesized over the Range 5–100 Nm Using the Same Protocol and Their Antibacterial Efficacy." *RSC Adv*. 4.8 (2014): 3974–3983.

18. Levard, C., Hotze, E. M., Lowry, G. V., & Brown, G. E. (2012). Environmental Transformations of Silver Nanoparticles: Impact on Stability and Toxicity. *Environmental Science & Technology*, *46*(13), 6900–6914.

19. Louie, S. M., Gorham, J. M., McGivney, E. A., Liu, J., Gregory, K. B., Hackley, V. A., … Parak, W. J. (2016). Photochemical transformations of thiolated polyethylene glycol coatings on gold nanoparticles. *Environ. Sci.: Nano*, *3*(5), 1090–1102.

20. Yin, Yin, Yongguang et al. "Particle Coating-Dependent Interaction of Molecular Weight Fractionated Natural Organic Matter: Impacts on the Aggregation of Silver Nanoparticles." *Environmental Science and Technology* 49.11 (2015): 6581–6589.

21. Y Li, Yang et al. "Surface-Coating-Dependent Dissolution, Aggregation, and Reactive Oxygen Species (ROS) Generation of Silver Nanoparticles under Different Irradiation Conditions." Environmental Science and Technology 47.18 (2013): 10293–10301.

22. Li, Xuan, and John J Lenhart. "Aggregation and Dissolution of Silver Nanoparticles in Natural Surface Water." Environmental Science and Technology 46.10 (2012): 5378–5386.

23. Kumar, R., Howdle, S., & Münstedt, H. (2005). Polyamide/silver antimicrobials: Effect of filler types on the silver ion release. *Journal of Biomedical Materials Research Part B: Applied Biomaterials*, *75B*(2), 311–319.

24. Liu, Jingyu, and Robert H. Hurt. "Ion Release Kinetics and Particle Persistence in Aqueous Nano-Silver Colloids." *Environmental Science and Technology* 44.6 (2010): 2169–2175.

25. Gri Grillo, Renato, André H Rosa, and Leonardo F Fraceto. "Engineered Nanoparticles and Organic Matter: A Review of the State-of-the-Art." *Chemosphere* 2015: 608–619.

26. Gunsolus, I. L., Mousavi, M. P. S., Hussein, K., Bühlmann, P., & Haynes, C. L. (2015). Effects of Humic and Fulvic Acids on Silver Nanoparticle Stability, Dissolution, and Toxicity HHS Public Access. *Environ Sci Technol*, *49*(13), 8078–8086.

27. Yang, Xinyu et al. "Silver Nanoparticle Behavior, Uptake, and Toxicity in Caenorhabditis Elegans : Effects of Natural Organic Matter." *Environmental Science & Technology* 48.6 (2014): 3486–3495.

28. Yin Yin, Yongguang et al. "Particle Coating-Dependent Interaction of Molecular Weight Fractionated Natural Organic Matter: Impacts on the Aggregation of Silver Nanoparticles." *Environmental Science and Technology* 49.11 (2015): 6581–6589.

29. Amirbahman, Aria, and Terese M. Olson. "The Role of Surface Conformations in the Deposition Kinetics of Humic Matter-Coated Colloids in Porous Media." *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 95.2–3 (1995): 249–259.

30. Kaegi, Ralf et al. "Fate and Transformation of Silver Nanoparticles in Urban Wastewater Systems." Water Research 47 (2013): 3866–3877.

31. Kaegi, Ralf et al. "Behavior of Metallic Silver Nanoparticles in a Pilot Wastewater Treatment Plant." *Environmental Science & Technology* 45.9 (2011): 3902–3908. 7.

32. Liu, Jingyu, Kelly G. Pennell, and Robert H. Hurt. "Kinetics and Mechanisms of Nanosilver Oxysulfidation." *Environmental Science and Technology* 45.17 (2011): 7345–7353.

33. Derjaguin, B.V., and L. Landau. 1941. Theory of the stability of strongly charged lyophobic sols and of the adhesion of strongly charged particles in solutions of electrolytes. Acta Phys. Chim. URSS 14:633–662

34. Verwey, E., J. Overbeek, and K. van Nes. 1948. The theory of the stability of liophobiccolloids: The interaction of sol particles having an electric double layer. Elsevier, Amsterdam

35. Hotze, Ernest M, Tanapon Phenrat, and Gregory V Lowry. "Nanoparticle Aggregation: Challenges to Understanding Transport and Reactivity in the Environment." *Journal of Environmental Quality* 39 (2010): 1909–1924.

36. Stumm, W., and J.J. Morgan. 1996. Aquatic chemistry: Chemical equilibria and rates in natural waters. 3rd ed. John Wiley & Sons, New York.

37. Hug Hughes, Zak E et al. "Elucidating the Influence of Materials-Binding Peptide Sequence on Au Surface Interactions and Colloidal Stability of Au Nanoparticles." *Nanoscale* 9.1 (2017): 421–432.

38. Li, Li, Xuan, and John J Lenhart. "Aggregation and Dissolution of Silver Nanoparticles in Natural Surface Water." *Environmental Science and Technology* 46.10 (2012): 5378–5386.

39. Zhu, T., Lawler, D. F., Chen, Y., Lau, B. L. T., Cornelis, G., Yu, S., … Hsu-Kim, H. (2016). Effects of natural organic matter and sulfidation on the flocculation and filtration of silver nanoparticles. *Environ. Sci.: Nano*, *2*, 19–26.

40. Levard, Clément et al. "Sulfidation Processes of PVP-Coated Silver Nanoparticles in Aqueous Solution: Impact on Dissolution Rate." *Environmental Science and Technology* 45.12 (2011): 5260–5266.

41. Feiler, Adam A et al. "Adsorption and Viscoelastic Properties of Fractionated Mucin (BSM) and Bovine Serum Albumin (BSA) Studied with Quartz Crystal Microbalance (QCM-D)." Journal of Colloid and Interface Science 315 (2007): 475–481.

42. Rodahlfredrik, M., Krozerpeter, H., Kasemo, B., Rodahl, M., H&k, F., Krozer, A., … Kasemoa, B. (1995). Quartz crystal microbalance setup for frequency and Q-factor measurements in gaseous and liquid environments Quartz crystal microbalance setup for frequency and G!?-factor rneasurements in gaseous and liquid environments. *Citation: Review of Scientific Instruments Review of Scientific Instruments*, *66*(101).

43. Tamerler, C., Duman, M., Oren, E. E., Gungormus, M., Xiong, X., Kacar, T., … Sarikaya, M. (2006). Materials specificity and directed assembly of a gold-binding peptide. *Small*, *2*(11), 1372–1378.

44. Tamerler, C., Oren, E. E., Duman, M., Venkatasubramanian, E., & Sarikaya, M. (2006). AdsorTamerler et al. - 2006 - Adsorption Kinetics of an Engineered Gold Binding Peptide by Surface Plasmon Resonance Spectroscopy and a Quart-annotatedption kinetics of an engineered gold binding Peptide by surface plasmon resonance spectroscopy and a qua. *Langmuir : The ACS Journal of Surfaces and Colloids*, *22*(18), 7712–7718.

45. Xiao, Y., & Wiesner, M. R. (2012). Characterization of surface hydrophobicity of engineered nanoparticles. *Journal of Hazardous Materials*, *215*, 146–151.

46. Doktorovova, S., Shegokar, R., Martins-Lopes, P., Silva, A. M., Lopes, C. M., Müller, R. H., & Souto, E. B. (2012). Modified Rose Bengal assay for surface hydrophobicity evaluation of cationic solid lipid nanoparticles (cSLN). *European Journal of*

Pharmaceutical Sciences, *45*(5), 606–612.

47. Müller, R. H. (1991). *Colloidal carriers for controlled drug delivery and targeting : modification, characterization, and in vivo distribution*. Wissenschaftliche Verlagsgesellschaft.

48. Müller, R. H., Rühl, D., Lück, M., & Paulke, B. R. (1997). Influence of fluorescent labelling of polystyrene particles on phagocytic uptake, surface hydrophobicity, and plasma protein adsorption. *Pharmaceutical Research*, *14*(1), 18–24.

49. Levard, Clément et al. "Sulfidation Processes of PVP-Coated Silver Nanoparticles in Aqueous Solution: Impact on Dissolution Rate." *Environmental Science and Technology* 45.12 (2011): 5260–5266.

50. El El Badawy, Amro M. et al. "Impact of Environmental Conditions (pH, Ionic Strength, and Electrolyte Type) on the Surface Charge and Aggregation of Silver Nanoparticles Suspensions." *Environmental Science and Technology* 44.4 (2010): 1260–1266.

51. Al-Harbi, Laila M. et al. "Adsorpton of Polyvinylpyrrolidone over the Silica Surface: As Affected by Pretreatment of Adsorbent and Molar Mass of Polymer Adsorbate." *International Journal of Polymer Science* 2016 (2016): 1–9.

52. Ohshima, H. (2012). The Derjaguin-Landau-Verwey-Overbeek (DLVO) Theory of Colloid Stability. In *Electrical Phenomena at Interfaces and Biointerfaces* (pp. 27–34). Hoboken, NJ, USA: John Wiley & Sons, Inc.
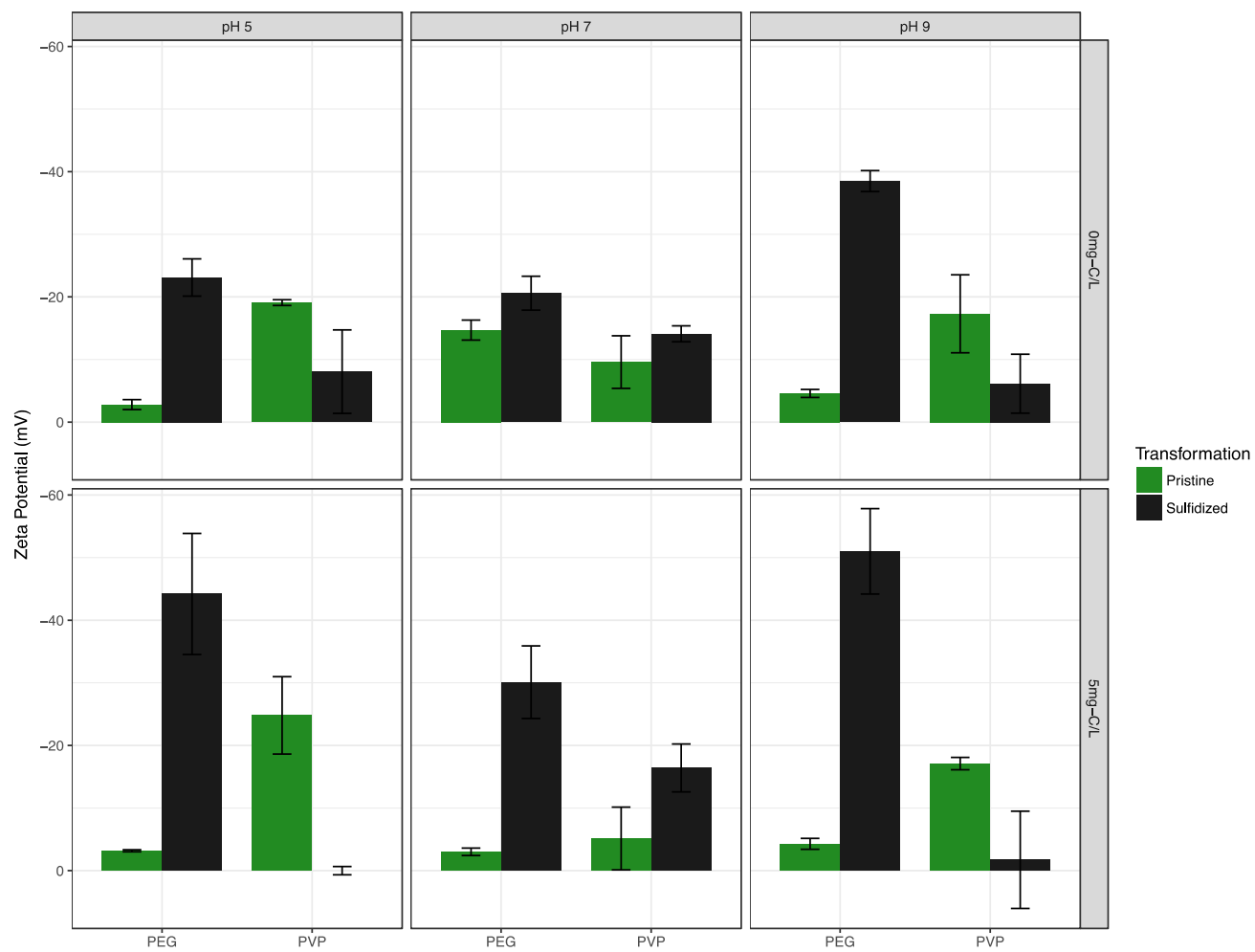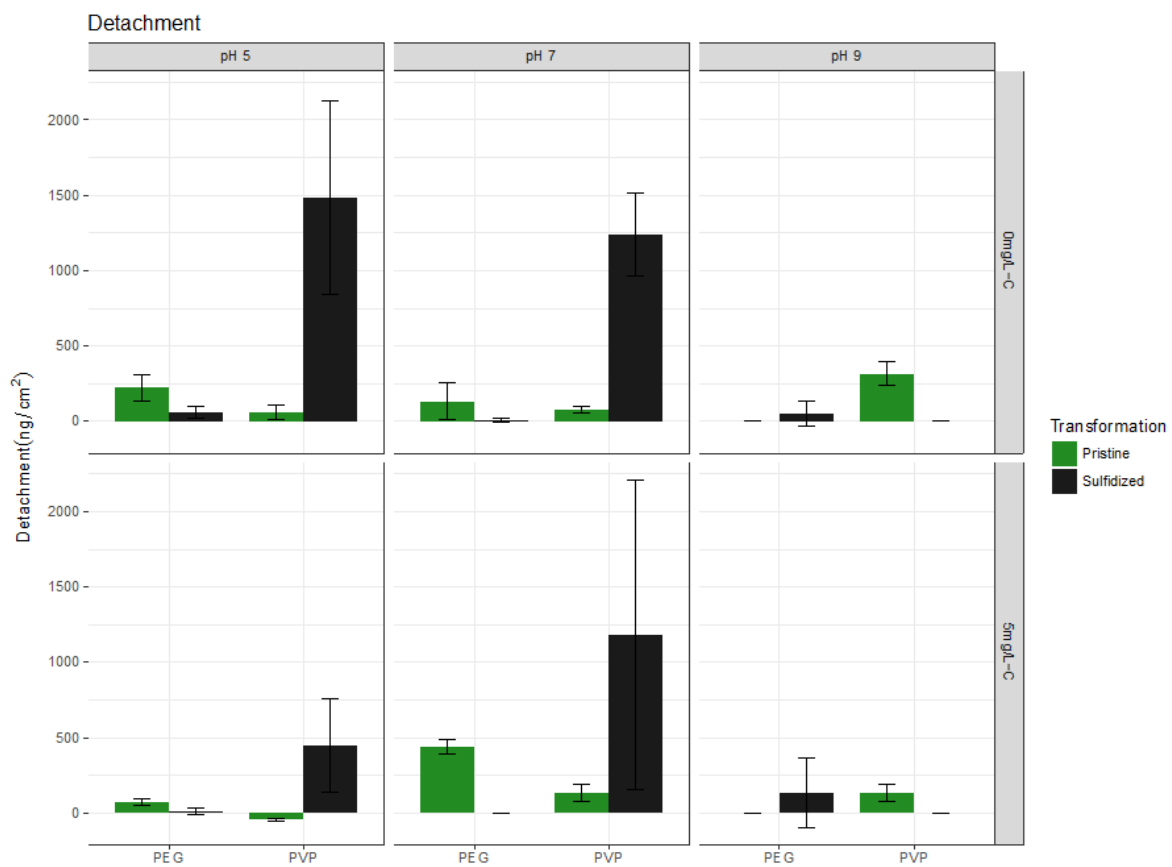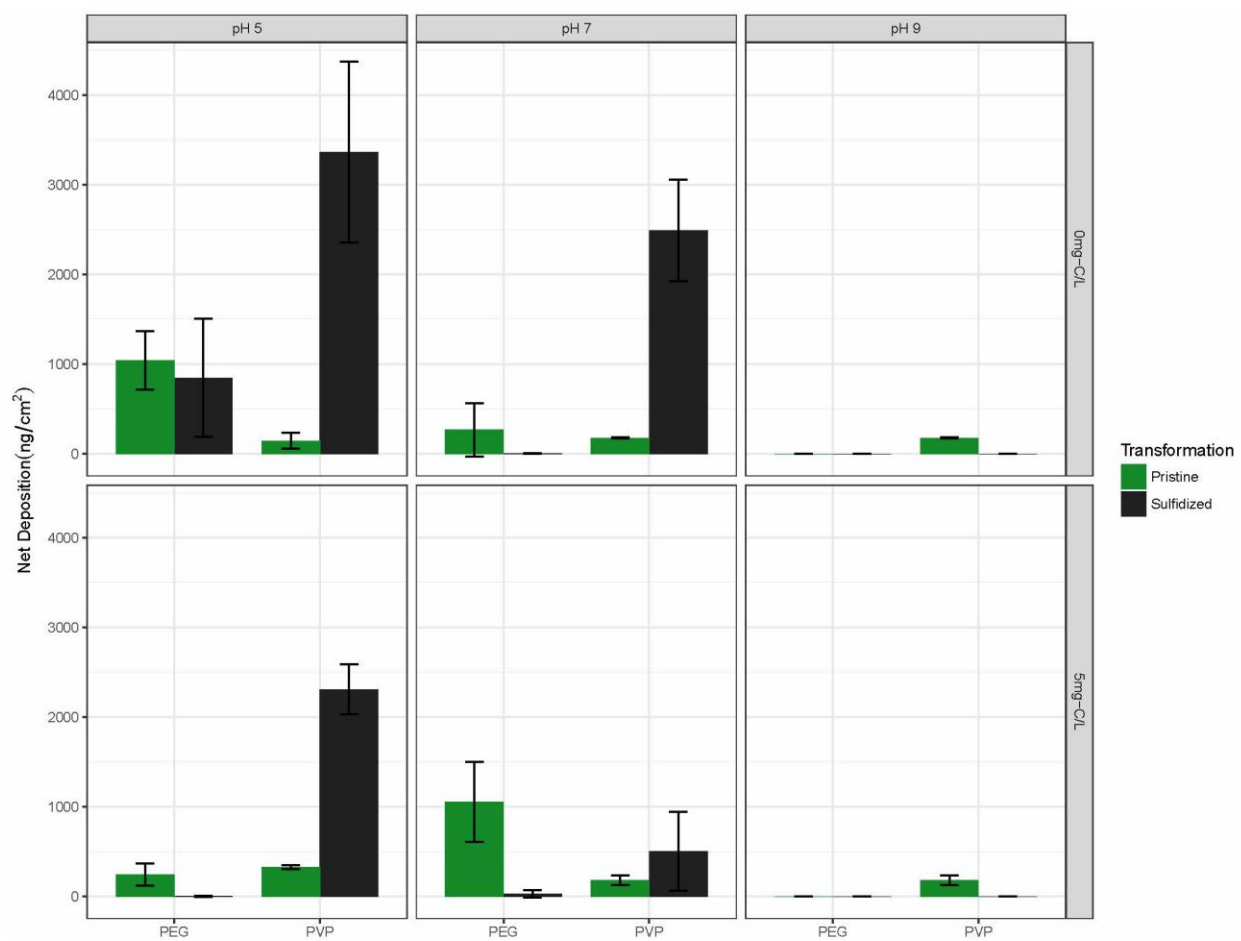
Appendices
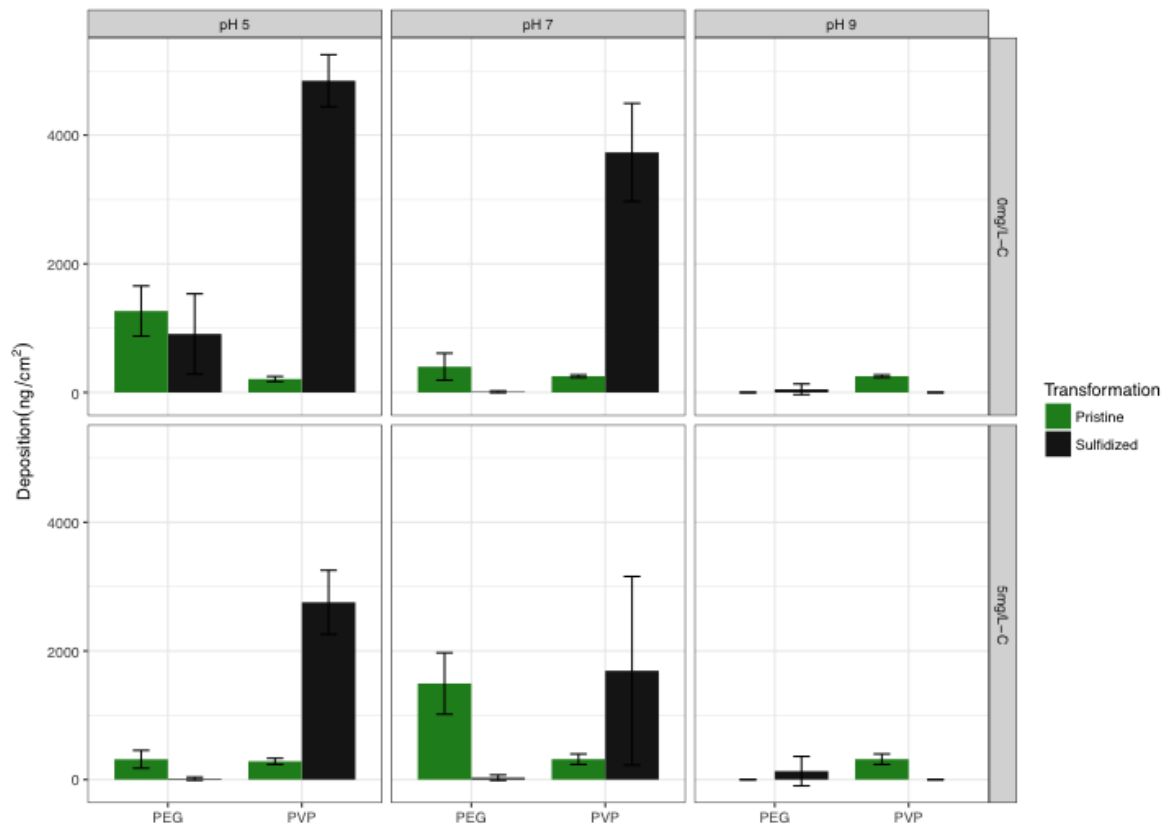
Appendix 1. Deposition extent of AgNPs.
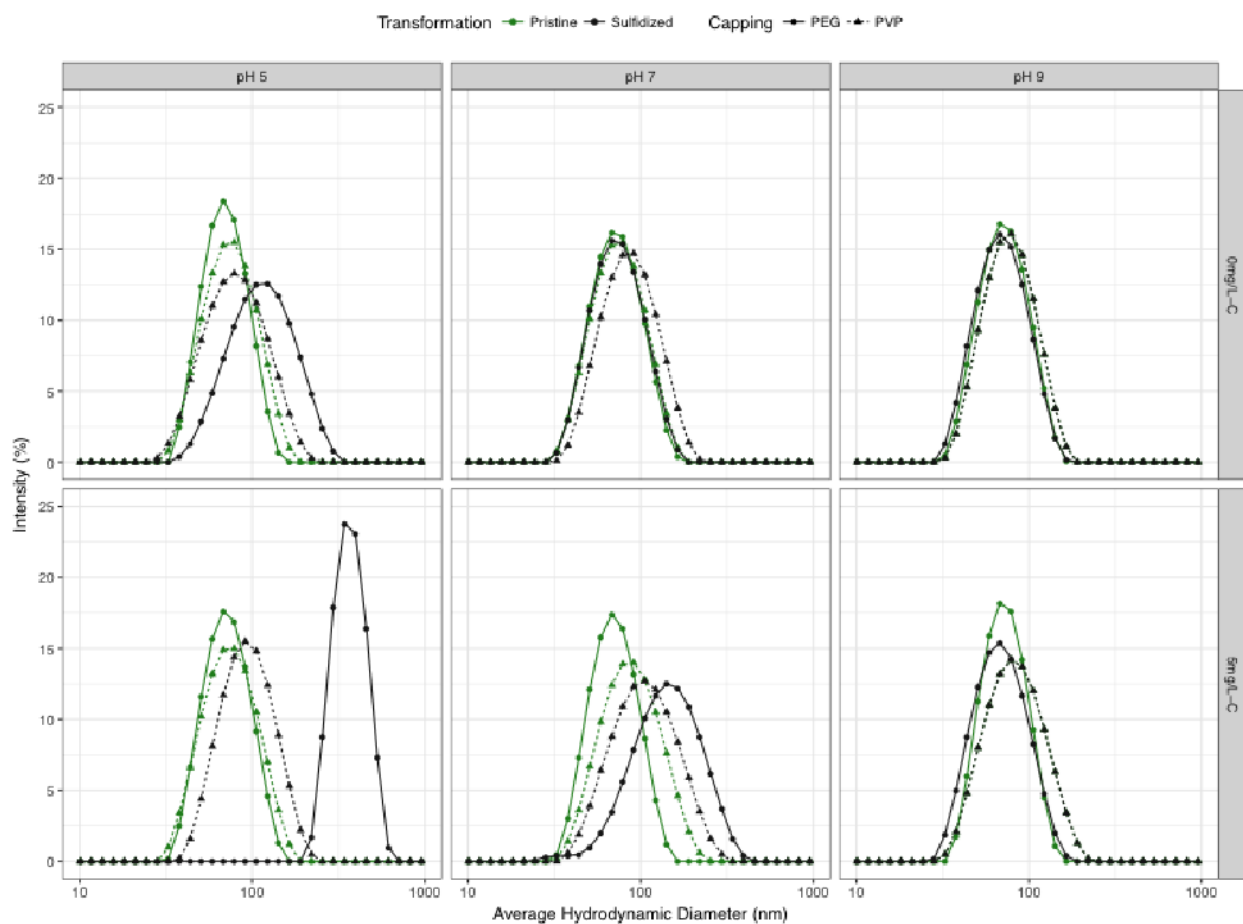
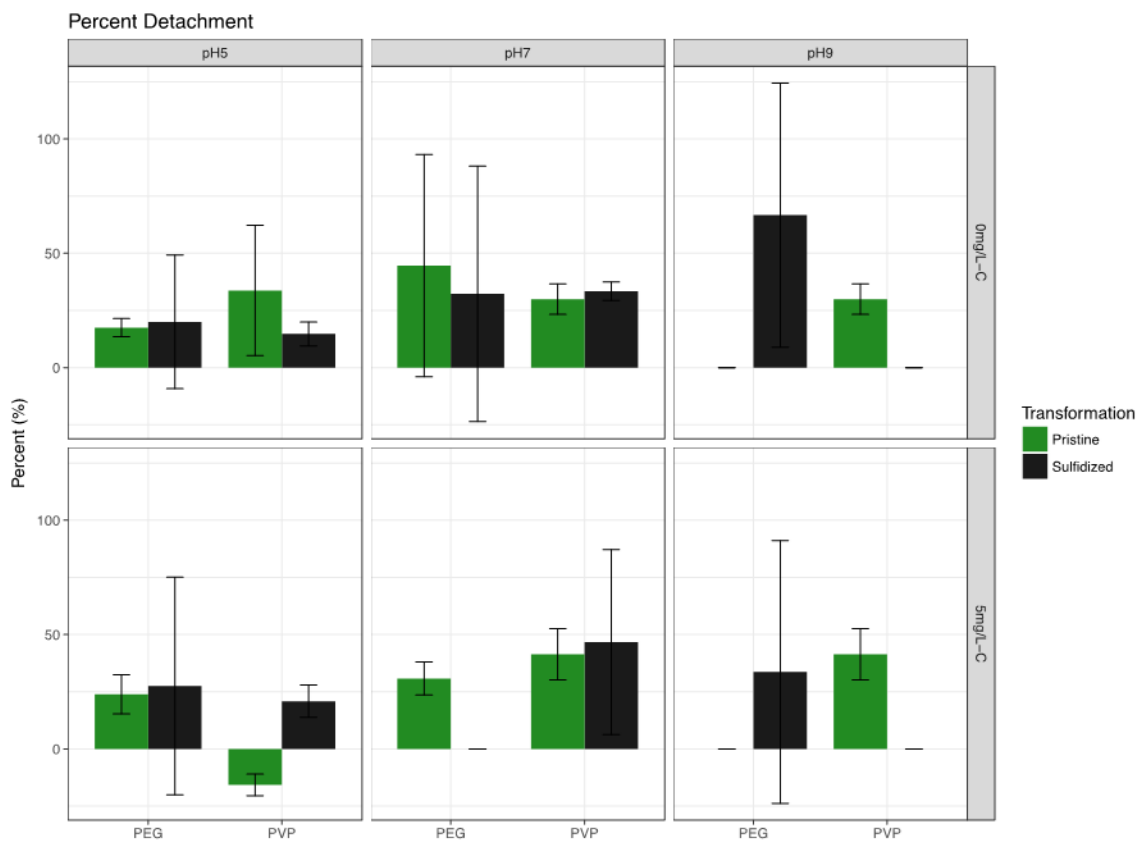**Appendix 2.** Particle Size Distribution of AgNPs.

Appendix 3. Zeta Potential (ZP) values of AgNPs.

Appendix 4. Detachment extent of AgNPs before and after sulfidation.

Appendix 5. The net deposition extent of AgNPs before and after sulfidation.

Appendix 6. Percent detachment before and after the sulfidation.