AN INVESTIGATION OF THE ADSORPTION BEHAVIOR BETWEEN SILVER NANOPARTICLES (AgNPs) AND CORUNDUM (α-Al₂O₃) AT ENVIRONMENTAL pH VALUES USING INDUCTIVELY-COUPLED PLASMA OPTICAL EMISSION SPECTROSCOPY (ICP-OES) AND RAMAN SPECTROSCOPY.

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By

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Kevin Andrew O’Neil ENTITLED An investigation of the adsorption behavior between silver nanoparticles (AgNPs) and corundum (α-Al₂O₃) at environmental pH values using inductively-coupled plasma optical emission spectroscopy (ICP-OES) and Raman spectroscopy BE ACCEPTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science.

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ABSTRACT

O’Neil, Kevin Andrew, M.S., Department of Chemistry, Wright State University. 2016. An investigation of the adsorption behavior between silver nanoparticles (AgNPs) and corundum (α-Al₂O₃) at environmental pH values using inductively-coupled plasma optical emission spectroscopy (ICP-OES) and Raman spectroscopy.

With the increased use of silver nanoparticles (AgNPs) in consumer products, the need to monitor their release into environmental soils has become critical. Although minerals make up a large component of soils, research on their interactions with AgNPs is still limited. Furthermore, the majority of the existing research focused on silica-based minerals rather than metal oxides, which is the second most abundant mineral type in the earth’s crust. This study examined for the first time the aqueous interaction between the widely used, spherical Creighton AgNPs and α-corundum (α-Al₂O₃), a representative non-silica-based mineral, at environmentally relevant pH values (6-11). Samples were prepared by incubating 100 mL of 1 mg L⁻¹ of AgNPs, ~1.182 g of α-Al₂O₃, 100 µL of 5 M of NaNO₃ as an ionic strength adjuster (ISA), and 100 µL of pH adjusters (0.1 M of HNO₃ or 0.1 M of NaOH) for 30 min. Samples were then centrifuged at 10,000 rpm for 2 min to separate the solid α-Al₂O₃ with bound AgNPs (pellet) from the aqueous portion containing free AgNPs (supernatant). The supernatant was then analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES) for the quantification of the total amount of AgNPs by difference adsorbed onto α-Al₂O₃. The pellet was placed on
glass microscope slides and large areas were mapped by micro-Raman spectroscopy in order to identify possible molecular interactions between AgNPs and α-Al₂O₃. The ICP-OES results demonstrated that over 75% of the available AgNPs were adsorbed to α-Al₂O₃ (sub-monolayer coverage), rapidly reducing their mobility in the environment. This sub-monolayer coverage was also verified using a total surface coverage value (Θ), with values ranging from 1.269×10⁻³ to 1.378×10⁻³. In addition, the adsorption process of the negatively charged Creighton AgNPs (in the 6-11 pH range) was found to be pH independent suggesting that other interaction mechanisms may counteract the electrostatic attractions (< pH 9) and repulsions (> pH 9) with corundum (pH_{pzc} = 9.1). The Raman images collected on the AgNP- α-Al₂O₃ samples (n = 1,089 spectra at each pH) revealed the appearance of an Ag-O stretching mode at 220-250 cm⁻¹, and confirmed the surface complexation of AgNPs to the terminus oxygen atoms (Ag-O-Al-). The highest chemisorption levels were statistically determined at pH ~ 9, when α-Al₂O₃ experiences loss of surface charge and is more readily available for direct molecular interactions with AgNPs. Overall, the results of this study demonstrate that both physisorption (electrostatic interactions) and chemisorption (other interactions such as hydrogen bonding, and London-dispersion forces) mechanisms play a role in the significant adsorption of Creighton AgNPs to α-Al₂O₃ and their reduced mobility into the environment at environmentally relevant pH values.
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INTRODUCTION

In the past decade, nanomaterials have become a greater part of consumer products (Figure 1A).\(^1\) The Woodrow Wilson Center for Emerging Nanotechnologies has recently shown that over 400 registered consumer products comprise silver nanoparticles (AgNPs), more than all other nanomaterials (Figure 1B).\(^1\) AgNPs are heavily used due to their unique antimicrobial,\(^2\) optical,\(^3\) and electrochemical properties.\(^4,5\) This increased exploitation is associated with potential problems posed to the environment due to the release of AgNPs into wastewater and landfills.\(^6\) Environmental concerns arise from uncertainty in the fate and the proven toxicity of AgNPs towards microorganisms\(^7\) and aquatic organisms.\(^8,9\) In general, the toxicity of AgNPs is attributed to the release of Ag\(^+\) ions under favorable redox conditions such as sunlight, dissolved organic matter, and pH.\(^10\) Both AgNPs\(^11,12\) and released Ag\(^+\) ions were reported to produce reactive oxidation species (ROS) and to induce oxidative stress on the organism.\(^13,14\) The fate of nanosilver in the environment remains disputed; it can exist in multiple forms: Ag\(^+\), AgNPs, and aggregated AgNPs.\(^15\) Nanosilver can also complex with other ions within freshwater and soils to create complexes such as silver sulfide (Ag\(_2\)S), silver cysteine, silver chloride (AgCl), silver fluoride (AgF), silver sulfate (Ag\(_2\)SO\(_4\)), silver hydroxide (AgOH), silver carbonate (Ag\(_2\)CO\(_3\)), or silver oxide (Ag\(_2\)O).\(^2,16\)
Current research suggests that released AgNPs are most likely to be immobilized in soils due to the adsorption and complexation to natural organic matter (NOM) and minerals, respectively.\textsuperscript{17–19} Most of these studies focus on AgNPs adsorption to NOM because of the high affinity of AgNPs to the sulfhydryl rich functional groups, which are commonly present in NOM.\textsuperscript{20–22} However, NOM only makes up ~ 5% of soil on average; therefore,\textsuperscript{23} it is also important to examine the interaction of AgNPs with the main component of soils, namely minerals. Minerals make up ~ 45% of most soils, while water and air take up the rest.\textsuperscript{23} Currently, there is extensive research available on the interactions between metal ions and soil minerals, but only few studies were reported on nanometals.\textsuperscript{24–26} Moreover, the research that does exist on AgNPs is generally focused on the interactions with silica-based minerals (\textit{i.e.}, SiO\textsubscript{2}),\textsuperscript{27,28} because these minerals are the

\textbf{Figure 1.} A) Number of consumer products containing nanoparticles from the years 2005 to 2013.\textsuperscript{1} B) Number of consumer products containing each type of nanoparticle.\textsuperscript{1}
most abundant in the earth’s crust (49.5 % for silicon and 25.7 % for oxygen). These experiments suggested that AgNPs can adsorb to clay minerals (which mostly contain Si$_x$O$_y$) if it has been first converted to Ag$^+$ and interact more with polar silica minerals than less polar ones. However, the interaction mechanisms of AgNPs with non-silica-based minerals remain largely unexplored.

This project examines the interaction between the Creighton AgNPs and a representative non-silica-based mineral, $\alpha$-Al$_2$O$_3$, at environmentally relevant pH values (6-11). Lowering the pH below 6 led to a large flocculation of these AgNPs. The Creighton synthesis is one of the most widely-used bottom-up fabrication approach of colloidal AgNPs due to its simplicity, time and cost efficiency. In this study, an AgNP concentration of 1 mg L$^{-1}$ was selected in order to ensure sub-monolayer coverage at the $\alpha$-Al$_2$O$_3$ surface and to surpass the maximum contaminant level (MCL) set by the U.S. Environmental Agency (EPA) for Ag$^+$ in drinking water caused from both natural and anthropogenic reasons (0.1 mg L$^{-1}$). $\alpha$-Al$_2$O$_3$ was chosen as the mineral model because it contains aluminum, which is the third most abundant element in the earth’s crust, after oxygen and silicon. Additionally, $\alpha$-Al$_2$O$_3$ has a pH pristine point of zero charge (pH$_{ppzc}$) of 9.1 that is close to the pH of 8.2 for Creighton AgNPs (Zeta potential of -44.7 mV). Thus, at typical pH values of soils (3.5-9), these negatively charged AgNPs are expected to experience a stronger physical interaction with $\alpha$-Al$_2$O$_3$. 


Two well-established analytical techniques were adapted in order to examine for the first time the AgNP- α-Al₂O₃ interaction with high reproducibility and sensitivity. Inductively coupled plasma optical emission spectroscopy (ICP-OES) quantified the total amount of AgNPs adsorbed to α-Al₂O₃ down to the low ppb level and helped estimate their total surface coverage (Θ). Micro-Raman spectroscopy-based mapping of large sample sizes in combination with chemometric approaches image the distribution of AgNPs onto the α-Al₂O₃ surface and identified other potential interaction mechanism(s) at the molecular level.

MATERIALS AND METHODS

Synthesis of AgNPs: Aqueous colloidal AgNPs were produced via a Creighton method in an ice bath (Figure 2). The synthesis utilizes a slightly modified 2:1 mM ratio of sodium borohydride (300 mL of 99% ACS fragment grade NaBH₄) to silver nitrate (50 mL of 99.8 % ACS trace metal grade AgNO₃) in order to increase the stability of the aqueous colloid. After adding AgNO₃ to NaBH₄ in a drop wise manner, the stirring was continued to ensure the reduction of Ag⁺ ions and formation of AgNPs. The final colloid had a yellow color and was stable for about 4 months.
Figure 2. A) Synthesized Creighton AgNP showing characteristic transparent yellow color. B) Setup of titration synthesis of Creighton AgNPs.

*UV/Visible (Vis) absorption spectrophotometry of AgNPs:* The formation of spherical AgNPs was confirmed by the presence of a localized surface plasmon resonance (LSPR) via a Varian Cary 50 Ultraviolet-Visible (UV/Vis) spectrophotometry (Figure 3). The colloidal samples were measured in disposable 2-mL cuvettes of a path length of 1 cm.
Preparation of AgNP-α-Al₂O₃ samples: AgNPs (100 mL of 1 µg mL⁻¹ of nanocolloid) were mixed with α-Al₂O₃ (1.1822 g of 99% Al₂O₃ purchased from Alfa Aesar), sodium nitrate as an ionic strength adjuster (ISA) (100 µL of 5 M of NaNO₃), and varying amounts of pH adjusters, (0.1 M of HNO₃ or as (0.1 M of sodium hydroxide (NaOH)). A SevenGo Duo pro model pH meter was used to measure the pH. After stirring for 30 min,
the samples were centrifuged for 2 min at 10,000 RCF in an AccuSpin Micro 17/17R model centrifuge. The supernatant was then decanted and used for the ICP-OES quantification of the Ag content, while the solid pellet was analyzed by Raman spectroscopy by creating a smear on a quartz microscope slide.

*Inductively coupled plasma optical emission spectrometer (ICP-OES) of AgNPs, α-Al₂O₃, and AgNP-α-Al₂O₃:* Quantitative characterization of the Ag content was done by a Varian 710 ICP-OES (Figure 4). Briefly, 1 mL of AgNP samples were digested in 2 mL of OPTIMA grade nitric acid (70 % HNO₃) to less than 200 µL and were then diluted in a 2 % HNO₃ matrix. Samples of α-Al₂O₃ interacted with AgNPs were prepared by mixing 1.1822 g with 100 mL of AgNPs for 30 min. Then a 2 mL aliquot was centrifuged at 10,000 rpm for 2 min. The supernatant was then removed and 1 mL was digested in 70% HNO₃ to less than 200 µL and diluted to a 2% HNO₃ matrix. A control sample of α-Al₂O₃ by itself was prepared in an identical fashion replacing the 100 mL of AgNPs with the same amount of high quality (HQ) water. Samples were then analyzed via an ICP-OES instrument equipped with an autosampler that peristaltically pumped the sample into a Meinhard nebulizer at a rate of 2 mL min⁻¹. A continuous argon gas flow aspirated the sample through the nebulizer at a flow rate of 15.0 L min⁻¹. Samples were measured in triplicate with a read time of 15 s and an instrument stabilization delay of 40 s using an axially positioned quartz torch at the two most intense Ag emission wavelengths (328.068 nm and 338.289 nm). Ag⁺ standards were prepared by diluting to a 2% matrix using HQ water from a 1,000 mg L⁻¹ of Ag⁺ SPEX CentriPrep stock standard. A seven
point calibration curve (0, 5, 10, 15, 20, 25, 50, 75, 100, 125, and 150 µg L⁻¹) was constructed via the external calibration method and samples were interpolated to determine their concentrations.

**Figure 4.** Picture of Varian 710 CP-OES instrument used and located in 069 Brehm Lab hall at Wright State University, Dayton, Ohio.

*Raman spectroscopy of AgNPs, α-Al₂O₃, and AgNP-α-Al₂O₃:* This analytical technique was employed to verify the purity of AgNPs and α-Al₂O₃, and to examine their possible molecular interactions (Figure 5). Aliquots of ~ 2 mL of colloidal AgNPs were analyzed in a quartz cuvette with the help of a LabRam HR 800 Raman spectrometer.
coupled to an Olympus 50 X objective. The resulting centrifuged pellets containing the α-Al₂O₃ control were analyzed on a glass slide with the Olympus 100 X objective. All spectra were acquired at the 532.134 nm excitation wavelength using a thermoelectrically cooled Andor CCD camera of 1024 x 256 pixels. The following instrumental parameters were selected for the acquisition of the Raman data: confocal hole of 300 µm, a holographic grating of 600 grooves mm⁻¹, acquisition times of 3 s, and 3 cycles. Under these conditions, the spectral resolution was ~ 1.2 cm⁻¹. Smears of the centrifuged pellets containing the AgNPs interacted with α-Al₂O₃ were made on glass slides and randomly selected 11-µm X 11-µm areas were Raman-mapped in order to obtain a more representative molecular picture of the surface interaction. For each pH, three individually prepared samples were made and three maps were ran for each sample making nine maps in total for each pH (n=1089 spectra in total). As opposed to conventional point spectra, Raman imaging uses a motorized stage to scan the surface in two dimensions and to effectively collect multiple point spectra of the sample with 1-µm² spatial resolution. The collected point spectra on the control AgNPs and α-Al₂O₃ were evaluated in Origin 8 software. Due to the larger amount of sample spectra, Raman data was managed and processed in Vespucci: an open-source, free software specifically designed by one of the authors for the hyperspectral analysis of Raman datasets.³⁵
Figure 5. Image of the LabRam 800 Raman system located in 458 Oelman Hall at Wright State University, Dayton, Ohio.

Raman data analysis: Spectra were median filtered (window size 7) and normalized so that the maximum intensity value of each spectra was 1 and the minimum intensity value was 0. Peak centers and integrated areas were found for the range from 220–250 cm\(^{-1}\) using a program written using the Vespucci C++ API.\(^{35}\) A linear baseline was drawn between the two abscissa values closest to the specified range. The area of the region was taken to be the sum of the difference of all values in the range and the local linear baseline, scaled by the width of the region. Peak centers were taken to be the abscissa value of the highest intensity point in the range after baseline subtraction. Post-processing of the results was performed using Version 8 of the SAS software.
RESULTS AND DISCUSSION

*Synthesis and characterization of AgNPs:*

Several batches of Creighton AgNPs (2 L) were successfully synthesized. The formation of AgNPs was confirmed by the appearance of a transparent yellow color and the appearance of a sharp, symmetrical surface plasmon resonance peak at 401 nm in the UV/Vis absorption spectrum (Figure 6). Raman spectroscopy confirmed the purity of the synthesized AgNPs (Figure 7); only three bands characteristic to the scissoring bending, symmetric stretching, and asymmetric stretching of water were detected at 1640 cm\(^{-1}\), 3241 cm\(^{-1}\), 3394 cm\(^{-1}\), respectively. Chemically digested AgNPs were quantified for total Ag employing an interpolated 8-point external calibration curve via ICP-OES. Total Ag concentration was revealed to be 17.27 mg L\(^{-1}\). Our group has previously shown by TEM that these AgNPs are spherical, have an average diameter of 11.0 nm ± 4.6 nm, and a moderate size distribution.\(^{36}\) In our previously published work, Zeta-potential measurements were able to demonstrate these AgNPs are negatively charged and stable at the experimental pH range.\(^{36}\) More specifically, the Zeta-potential varied from -45.0 mV to -61.3 mV in the 6.6 to 10.3 pH range. X-ray near edge spectroscopy (XANES) measurements performed on the GSECARS beamline, by my colleague Seth Brittle, at the Advanced Photon Source in Argonne national laboratory showed no oxidation on the surface of the original Creighton AgNPs.\(^{37}\)
Figure 6. UV/VIS absorption spectrum of Creighton AgNPs illustrating their surface plasmon resonance peak at 401 nm.
Figure 7. Raman spectrum indicating a lack of impurities in the Creighton AgNPs.

Characterization of $\alpha$-$\text{Al}_2\text{O}_3$.

The $\alpha$-$\text{Al}_2\text{O}_3$ used in this experiment exhibits a specific surface area of 6-8 m$^2$ g$^{-1}$ (Alfa Aesar). In addition, further characterization was done via ICP-OES and Raman spectroscopy. No silver impurities were revealed by ICP-OES analysis and Raman spectroscopy analysis. Control ICP-OES analysis was done by the same method at samples (see materials and methods) substituting 100 mL of 1 mg L$^{-1}$ AgNPs for 100 mL...
of high quality H₂O. Control Raman spectra indicate six characteristic peaks of α-Al₂O₃ at 378 cm⁻¹, 416 cm⁻¹, 429 cm⁻¹, 451 cm⁻¹, 576 cm⁻¹, 644 cm⁻¹, and 750 cm⁻¹ (Figure 8). Each peak was assigned according to the literature (Table 1). The bands at 378 cm⁻¹ and 429 cm⁻¹ indicates the E₉ internal stretching mode, 416 cm⁻¹ and 644 cm⁻¹ correspond to the A₁₉ stretching mode, and 451 cm⁻¹, 576 cm⁻¹, and 750 cm⁻¹ indicate E₉ internal stretching modes for the Al-O bonds. 

Taking into account the average AgNP diameter estimated from TEM, an experimental mass of 1.1822 g of α-Al₂O₃ was calculated as being necessary for a sub-monolayer coverage of the α-Al₂O₃. Equation 1 shows the equation for finding the number of nanospheres in the AgNPs,

\[
n = \frac{[\text{AgNP}]_{\text{ICP}} \times V}{\frac{4}{3} \times \pi \times r^3 \times \rho_{\text{Ag}}} \quad [1]
\]

where \(n\) is the number of nanospheres, \([\text{AgNP}]_{\text{ICP}}\) is the concentration (1 mg L⁻¹), \(V\) is the volume used, and the bottom of the fraction represents the density of Ag multiplied by the volume of a nanosphere. In Equation 2, the total area of the surface was found,

\[
SA_c \times M_c = \text{total} \ A_s \quad [2]
\]

where \(SA_c\) is the surface area of α-Al₂O₃, \(M_c\) is the mass of α-Al₂O₃, and \(A_s\) is the total area of the surface. The number of nanospheres can then be related to the mass of corundum in Equation 3.
\[ n = \frac{SA_c}{4 \times \pi \times r^2} \times M_c \]  \hspace{1cm} [3]

Substituting this for \( n \) in Equation 1 and solving for the mass of corundum yields the following relationship.

\[ M_C = \frac{3 \times [AgNP]_{ICP} \times V}{\pi r^2 \rho_{Ag} \times SA_c} \]  \hspace{1cm} [4]

This equation yields a value of 1.1822 g of \( \alpha \)-Al\(_2\)O\(_3\) needed to ensure a sub-monolayer coverage by AgNPs.
Figure 8. Raman spectrum of $\alpha$-Al$_2$O$_3$ (1.0 $\mu$m in diameter) purchased from Alfa Aesar.
Table 1. Tentative assignments of the Raman vibrational modes observed for $\alpha$-Al$_2$O$_3$.

<table>
<thead>
<tr>
<th>Experimental Raman modes (cm$^{-1}$)</th>
<th>Literature Raman Shift (cm$^{-1}$)</th>
<th>Tentative assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>378 ($m$)</td>
<td>378$^{38-42}$</td>
<td>$E_g$ external</td>
</tr>
<tr>
<td>416 ($s$)</td>
<td>416$^{38-42}$</td>
<td>$A_{1g}$</td>
</tr>
<tr>
<td>429 ($m,sh$)</td>
<td>429$^{38-42}$</td>
<td>$E_g$ external</td>
</tr>
<tr>
<td>451 ($w$)</td>
<td>451$^{38-41}$</td>
<td>$E_g$ internal</td>
</tr>
<tr>
<td>574-576 ($w$)</td>
<td>576$^{38-42}$</td>
<td>$E_g$ internal</td>
</tr>
<tr>
<td>644 ($m$)</td>
<td>644$^{38-42}$</td>
<td>$A_{1g , \perp}$</td>
</tr>
<tr>
<td>750 ($m$)</td>
<td>750$^{38-42}$</td>
<td>$E_g$ internal</td>
</tr>
</tbody>
</table>

Abbreviations: vs – very strong, $s$ – strong, $m$ – medium, $w$ – weak, $sh$ – shoulder.

Characterization of AgNP/$\alpha$-Al$_2$O$_3$ interaction.

The addition of 1.1822 g of $\alpha$-Al$_2$O$_3$ to 100 mL of 1 mg L$^{-1}$ AgNPs immediately altered the slightly transparent yellow AgNPs to an opaque milky white. After the 30-min incubation period, 2 mL aliquots were centrifuged and measured by ICP-OES and Raman spectroscopy. The pH values before and after incubation with AgNPs for 30 min differed only slightly ($\sim \pm 0.1$ pH unit). However, preliminary work performed by our group (not published yet) indicated that incubation times longer than 30 min may lead to more significant pH changes especially at higher pH values (pH 9-11) due to formation of carbonic acid with the CO$_2$ in the air.
ICP-OES: The total Ag remaining in supernatant was determined using ICP-OES. Ag adsorbed to the $\alpha$-$\text{Al}_2\text{O}_3$ surface was estimated from the difference between the starting AgNP concentration (~1 mg L$^{-1}$ of AgNPs) and the total AgNP concentration of the measured supernatant sample (unbound AgNPs). Dividing the starting AgNP concentration by the adsorbed concentration yields the total % AgNPs adsorbed (Eq. 5).

$$\% \text{ AgNP Adsorbed} = \frac{[\text{AgNP}_{\text{Adsorbed}}]}{[\text{AgNP}_{\text{Initial solution}}]} \times 100\% \quad [5]$$

ICP-OES data showed that over 75% of the available AgNPs were adsorbed to the $\alpha$-$\text{Al}_2\text{O}_3$ surface at all pH values (Figure 9). Furthermore, no significant pH dependence was determined in the AgNP adsorption level as a function of pH (Figure 9). This may be indicative of multiple adsorption mechanisms occurring at the $\alpha$-$\text{Al}_2\text{O}_3$ surface, including electrostatic attraction, surface complexation, and hydrogen bonding.
**Figure 9.** Percent AgNPs adsorption to α-Al₂O₃ as a function of pH as determined by ICP-OES. Error bars represent standard deviation of nine independently prepared samples.

Previously cited literature has shown the hydration of α-Al₂O₃ yields OH groups at the Al₂O₃ surface, thus the interaction between AgNPs and α-Al₂O₃ is expected to involve hydroxyl groups.⁴³ This hydroxyl group will also undergo deprotonation at the pzc of α-
Al₂O₃ to create an overall negative charge above pH 9.⁴⁴ At pH values > 9, the α-Al₂O₃ surface consists of OH- moieties that produce an overall negative surface charge, which will undergo electrostatic repulsions with the negatively charged AgNPs. Thus, less overall AgNP adsorption is expected at pH values > 9 than at all other investigated pH values. However, as seen in Figure 10, AgNPs can still bind to surface moieties that are not negatively charged due to the other possible mechanisms (e.g., surface complexation or hydrogen bonding⁴⁵ interactions). Moreover, the introduction of Na⁺ ions (from the NaNO₃ salt added) can bind to these negatively charged moieties as well as the oxygen itself, creating a potential for AgNPs to be more attracted. The surface complexation mechanism is described below in the Raman spectroscopy data analysis. AgNPs also undergo slight oxidation at these pH values,⁴³,⁴⁶,⁴⁷ which may further justify the over 80% adsorption levels (Figure 9).
Figure 10. Proposed complexation scheme between Creighton AgNPs and α-Al₂O₃ at pH values > 9 (drawing not to scale). Red circles = Aluminum, blue = oxygen, yellow = sodium, and gray = hydrogen.

At pH ~ 9, all of the previously mentioned mechanisms are at play again due to the absence of charge in some surface moieties as well as the presence of both positive and negative moieties as well as the Na⁺ interactions (Figure 11). Negatively charged AgNPs
will experience electrostatic attractions with the positive surface sites and electrostatic repulsion with the negative surface sites of $\alpha$-Al$_2$O$_3$.

**Figure 11.** Proposed complexation scheme between Creighton AgNPs and $\alpha$-Al$_2$O$_3$ at pH values ~ 9 (drawing not to scale). Red circles = Al, blue = oxygen, yellow = sodium, and gray = hydrogen.
At pH values < 9, electrostatic attractions are more likely due to the increased number of positive charged $\alpha$-Al$_2$O$_3$ surface sites that may interact with the negatively charged AgNPs (Figure 12). Moreover, surface complexation and hydrogen bonding are still relevant adsorption mechanisms for the same reasons stated above. Interactions with Na$^+$ on the surface only occurs at pH 8 (pH 6 and 7 had no Na added). However, as the pH starts approaching more acidic values, the AgNPs have an increased chance of oxidation into Ag$^+$, which in turn may decrease the total AgNP adsorption.
**Figure 12.** Proposed complexation scheme between Creighton AgNPs and $\alpha$-Al$_2$O$_3$ at pH values $< 9$ (drawing not to scale). Red circles = Al, blue = oxygen, yellow = sodium, and gray = hydrogen.

Although an effective simplified representation for the purpose of this experiment, the percent adsorbed values for each pH does not consider specific surface area of the AgNPs...
and $\alpha$-Al$_2$O$_3$. Alternatively, AgNPs adsorption can be thought of in terms of surface area. Since AgNPs are larger than a surface site on $\alpha$-Al$_2$O$_3$ the total surface area footprint AgNPs can occupy and do occupy can be compared. In other words, the concentration can be converted to molarity, then to the total number of Ag atoms, followed by the number of nanospheres, and finally converted to a total surface area AgNP can/do occupy ($i.e.$, their footprint).

First, a cross-sectional average area was determined from the average TEM diameter (Eq. 6).

$$A_{\text{nanosphere}}: A = \pi r^2, A = (5.5 \text{nm})^2 \pi = 95.0 \text{nm}^2 = 9.50 \times 10^{-17} \text{m}^2 \quad [6]$$

Next, the total number of Ag atoms (within TEM ranges) that are contained in one Ag-nanosphere was determined (Eq. 7).

$$V = \left(\frac{4}{3}\right) \pi (5.5 \times 10^{-9} \text{m})^3 = 6.97 \times 10^{-25} \text{m}^3 \quad [7]$$

Then the total number of Ag atoms in 100 mL of 1 mg L$^{-1}$ AgNP was calculated (Eq. 8)

$$\frac{1 \times 10^{-3} \text{g Ag}^+}{1 \text{L}} \times \frac{1 \text{mol}}{107.86 \text{g Ag}^+} \times \frac{6.02 \times 10^{23} \text{Ag atoms/mol}}{\text{mol}} = 5.58 \times 10^{18} \text{Ag atoms L}^{-1} \quad [8]$$

Using the density of silver ($D_{\text{Ag}} = 10.49 \text{g cm}^{-3}$), the mass for 1 nanosphere was found (Eq. 9).
Mass: \((1.049 \times 10^7 \text{ g m}^{-3}) \times (6.97 \times 10^{-25} \text{ m}^3) = 7.31 \times 10^{-18} \text{ g} \quad [9]\)

This mass can then be used to convert to number of Ag atoms (Eq. 10)

\[
7.31 \times 10^{-18} \text{ g} \times \frac{1 \text{ mol}}{107.86 \text{ Ag}^+} \times \frac{6.02 \times 10^{23} \text{ Ag atoms}}{\text{ mol}} = 40802 \text{ Ag atoms} \quad [10]
\]

Now the total number of Ag atoms is divided by the total number of atoms in a nanosphere (Eq. 11).

\[
\text{Number of nanospheres} = \frac{5.58 \times 10^{18} \text{ total Ag atoms}}{40802 \text{ atoms per sphere}} = 1.37 \times 10^{14} \text{ nanospheres} \quad [11]
\]

The total surface area of the AgNP footprint can then be calculated by multiplying the total number of Ag nanospheres by the cross sectional area (Eq. 12).

\[
SA = (9.50 \times 10^{-17} \text{ m}^2) \times 1.37 \times 10^{14} \text{ nanospheres} = 1.30 \times 10^{-2} \text{ m}^2 \quad [12]
\]

Total \(\alpha\)-\(\text{Al}_2\text{O}_3\) surface coverage \((\Theta)\) from AgNPs can then be calculated at each pH value using

\[
\Theta = \frac{\text{area occupied}}{\text{area available}} \quad [13]
\]

Where the area available is 8.28 m². Table 2 shows the average \(\Theta\) for each pH value.
Table 2. Total surface area footprint by the AgNPs used to calculate the Θ of the AgNPs on the α-Al₂O₃ surface.

<table>
<thead>
<tr>
<th>pH</th>
<th>total AgNP surface area (m²)</th>
<th>Θ</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>1.051E-02</td>
<td>1.269E-03</td>
</tr>
<tr>
<td>7</td>
<td>1.053E-02</td>
<td>1.272E-03</td>
</tr>
<tr>
<td>8</td>
<td>1.138E-02</td>
<td>1.375E-03</td>
</tr>
<tr>
<td>9</td>
<td>1.141E-02</td>
<td>1.378E-03</td>
</tr>
<tr>
<td>10</td>
<td>1.123E-02</td>
<td>1.357E-03</td>
</tr>
<tr>
<td>11</td>
<td>1.074E-02</td>
<td>1.297E-03</td>
</tr>
</tbody>
</table>

This calculation indicates sub-monolayer coverage of the α-Al₂O₃ surface. However, the Θ values do not indicate a large deviation in the total surface coverage of α-Al₂O₃ as a function of pH. To investigate further mechanisms of adsorption, Raman spectroscopy was employed.

Raman: Raman spectroscopy was utilized to examine possible molecular interactions between AgNPs and α-Al₂O₃. For each AgNP-α-Al₂O₃ sample smear, three Raman maps of 11 µm X 11 µm were acquired at each pH value and were processed in the Vespucci software. All Raman active points in the maps exhibited the six vibrational modes characteristic to α-Al₂O₃. These peaks had similar spectral profiles to those in the α-Al₂O₃ controls. Non-Raman active points in the maps had either no signal or the poor background signal corresponding to the glass support. Figure 13 displays representative AgNP-α-Al₂O₃ Raman spectra in comparison with the corresponding controls for AgNPs and α-Al₂O₃ at each pH value in the 6-11 range. A closer examination of these spectra shows the appearance of a new peak at 220-250 cm⁻¹ characteristic to the Ag-O
stretching\(^{48}\) (Figure 13). This mode is indicative of a direct molecular interaction between the negatively charged Creighton AgNPs and the terminus oxygen atoms on the corundum surface at all pH values. This **chemisorption** process results in the **surface complexation** of AgNPs through the formation Ag-O-Al complexes. The association of the Ag-O band with the pre-existence of an oxide layer to the AgNP surface was dismissed based on XAS measurements performed by my colleague Seth Brittle and our Wright-Patterson Air Force Base (WPAFB) collaborator, Dr. Sushil Kanel.

To offer both qualitative and semi-quantitative pictures of this interaction, Raman images were created from the Raman maps based on the baseline-adjusted integrated area of the Ag-O stretching mode from 220 to 250 cm\(^{-1}\). Sample Raman images and the corresponding color scales (green color pallet) are given for all pH values in Figure 14. It can be noticed that some of the pixels are silent, i.e., the corresponding Raman spectra did not exhibit an Ag-O mode or had poor signal-to-noise ratios. These points were color coded in dark green. All other pixels were assigned a color based on the integrated peak area of the Ag-O stretching mode with lightly colored regions corresponding to higher integrated area values. The number of these pixels marking the presence of Ag-O interactions between AgNPs and α-Al\(_2\)O\(_3\) were then quantified for each pH value (Figure 15). AgNPs were found to exhibit more interactions with α-Al\(_2\)O\(_3\) at pH ≥ 9 \((n = 901-1015\) spectra\) in comparison with all other examined pH values \((n = 796-814)\). This is in good agreement with the trend observed for the mean average of the integrated area
values of the Ag-O stretching band that was determined with 95% confidence at all pH values (Figure 16). However, there is a change in the general trend between pH 6 and 7, indicating a possible change in the interaction.

A box-and-whisker plot (Figure 17) of this same Ag-O region indicates that many of the pH values have outliers (anything outside three halves of the interquartile range). Moreover, the distributions overlap and indicate that the pH values are not normal. Statistical tests done by colleague Daniel Foose including the Dunn’s test and pairwise Mann-Whitney-Wilcoxon tests indicated statistical differences between the pH values shown in Table 3 (p<0.05 after Bonferroni adjustment). This indicates a pH-dependent effect in regards to the Ag-O interactions in the Raman signal.
Figure 13. Sample Raman spectrum at pH 6 showing the 230-240 cm\(^{-1}\) shift indicative of the presence of AgO (black). Control spectrum shown include AgNPs with ISA (red) and \(\alpha\)-Al\(_2\)O\(_3\) with ISA (blue), and indicate no presence of Ag-O.
**Figure 14.** Micro-Raman image of an 11 μm x 11 μm region illustrating the chemisorption of AgNPs to the corundum surface at pH 6-11 (A-F, respectively). The color scale was created based on the baseline-adjusted area of the Ag-O stretching mode signal from 220 to 250 cm⁻¹. Lightly colored regions have larger integrated area values.
Figure 15. The total number of Raman spectra exhibiting Ag-O stretching modes at each pH values.
Figure 16. Mean of the integrated area of the Ag-O stretching mode at each examined pH value with 95% confidence intervals. The values obtained at each pH represent an average of 1089 spectra from 3 separate trials.
Figure 17. Box and whisker plot of baseline-adjusted integrated area of the region between 220 and 250 cm$^{-1}$ at each pH value. Whiskers represent three halves of the interquartile range. Outliers outside three halves of the interquartile range are represented by circles.
Table 3. Statistical comparison indicating significant differences by pH.

<table>
<thead>
<tr>
<th>pH 1</th>
<th>pH 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
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</tbody>
</table>
CONCLUSIONS

ICP-OES and Raman spectroscopy-based imaging proved to be two powerful analytical techniques for the examination of the interaction mechanisms between Creighton AgNPs and α-Al₂O₃ at environmentally relevant pH values (6-11). ICP-OES revealed a large degree of adsorption, namely over 75% of the added AgNPs were adsorbed onto the α-Al₂O₃ surface. The sub-monolayer coverage with AgNPs was verified through the estimation of the total surface coverage value (θ values in the 1.269×10⁻³ to 1.378×10⁻³ range). However, the adsorption process of AgNPs to α-Al₂O₃ was found not to be pH dependent suggesting the physisorption of negatively charged AgNPs due to the attractions (< pH 9) or repulsions (> pH 9) with α-Al₂O₃ (pHₚzc = 9.1) is not the only mechanism playing a role in this adsorption behavior. The chemometric analysis of the large volumes of Raman data collected through 11 µm x 11 µm maps (n = 1089 spectra for each pH) showed that chemisorption also plays a role in the overall adsorption mechanism of AgNP. A new Ag-O stretching mode was detected at 220-250 cm⁻¹ at all pH values suggesting a surface complexation of AgNPs through the terminus oxygen atoms (Ag-O-Al-). Evaluations of the baseline-adjusted integrated area of the Ag-O peak showed that the highest degree of surface complexation occurred at pH ~ 9, close to the point of zero charge of α-Al₂O₃. Overall, this study demonstrates that both physisorption and chemisorption mechanisms play a role in the significant adsorption of Creighton AgNPs to α-Al₂O₃ and their reduced mobility into the environment at environmentally relevant pH values.
FUTURE DIRECTIONS

This work will be continued by future masters and/or Ph.D. students. These studies will focus on further investigating the role of pH by varying the concentration of AgNPs and ISA within each pH value. This will give further insight on the particular adsorption process in terms of a $K_{ads}$ value. Moreover, the study of different minerals will be conducted to attain more of an understanding of the AgNPs fate within soils.
References


(6) McLaughlin, M. J. 2013, 46 (3).


(35) Foose, D. P.; Sizemore, I. E. P. **2016**.


Curriculum Vitae

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RESEARCH EXPERIENCE

Graduate Research Assistant, Wright State University  
May 2014-Present

2. UV/Vis for the characterization of synthesized silver nanoparticles (AgNPs) for their use in mineral adsorption.
3. Raman spectroscopy and inductively-coupled plasma optical emission spectroscopy used for the investigation of AgNPs’ adsorption to corundum.
4. The characterization of pH dependent samples as well as the use of a pH meter used for the adsorption of AgNPs to corundum.

TEACHING EXPERIENCE

Graduate Teaching Assistant, Wright State University  
August 2014-Present

5. Quantitative analysis (CHM 3120) - Supervised the laboratory practices of undergraduate students performing titrations, dilutions, and various measurements on many different instrumental techniques.
6. Instrumental Analysis (CHM 4350) - Supervised the laboratory practices of students performing experiments using high-tech instruments involving many different technical processes.

SKILLS AND CERTIFICATIONS

Technical Skills: Preparation of samples to be used in spectroscopy analysis, synthesis of bottom-up silver nanoparticles, UV/Vis, flame atomic absorption spectroscopy, inductively-coupled plasma optical emission spectroscopy, and Raman spectroscopy.

Certifications: Currently certified by WSU’s Environmental Health and Safety Department in the following: Laser, Lab, and Radiation Safety Awareness.

PRESENTATIONS

Poster Presentation – 2014 Cleveland State Interdisciplinary Research Conference

_October 2014_

7. “Quantifying Silver within Nanocolloids by Inductively-Coupled Plasma Optical Emission Spectroscopy (ICP-OES) using Two Widely Accepted Calibration Methods”

_Kevin A. O’Neil, Seth W. Brittle, Joshua D. Baker, Kevin M. Dorney, Jessica M. Dagher, Tala Ebrahimian, Steven R. Higgins, and Ioana E. Sizemore_

Oral Presentation – 2015 National American Chemical Society in Denver

_March 2015_

8. “A Raman study of the adsorption behavior of silver nanoparticles at mineral and natural organic matter-water interfaces”

_Kevin A. O’Neil, Jessica L. Fraley, Seth W. Brittle, Jennifer M. Purvis, Sushil Kanel, Steven R. Higgins, Ioana E. Sizemore._

Oral Presentation – 2015 Wright State Celebration of Research

_April 2015_
9. “A study of the adsorption behavior of silver nanoparticles at corundum interfaces using Inductively-Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and Raman Spectroscopy”

Kevin A O’Neil, Seth W. Brittle, Jennifer M. Purvis, Steven R. Higgins, Ioana E. Sizemore.

Poster Presentation – 2015 Posters in the Hall at Wright State University
April 2015

10. “A study of the adsorption behavior of silver nanoparticles at corundum interfaces using Inductively-Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and Raman Spectroscopy”

Kevin A O’Neil, Seth W. Brittle, Jennifer M. Purvis, Steven R. Higgins, Ioana E. Sizemore.

Poster Presentation – 2016 Wright State Celebration of Research April 2016

11. “Adsorption behavior of positive and negatively charged silver nanoparticles to α-corundum as a function of pH”


RELAVENT COURSEWORK (Wright State University)
Undergraduate: Accelerated General Chemistry (CHEM 191), Inorganic Chemistry (CHEM 270), Organic Chemistry (CHEM 2400), Analytical Chemistry (CHEM 2800), Physical Chemistry (CHEM 3400), Instrumental Analysis (CHEM 3800), Biocemistry (BMB 4500)

Graduate: Introduction to Quantum Chemistry (Chm 7500), Chemical Kinetics (CHM 7520), Physical Organic Chemistry (CHM 7440), Advanced Inorganic Chemistry (CHM 7200), Electroanalytical Chemistry (CHM 6370), Chemical Processes in the Environment (CHM 7180)

EDUCATION

M. S., Chemistry, Wright State University May 2014-Present
Advisor: Ioana E. Sizemore
Current GPA: 3.689
Anticipated Graduation Date: May 2016

B. S., Chemistry, Otterbein University May 2014
GPA: 3.428