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Nanomaterial-Treated Filters for the Uptake of Heavy Metals from Water Sources

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Abstract

We describe the synthesis and properties of ligand-modified gold nanoparticles (AuNPs) grown on stainless steel wool filters. Their selectivity and efficiency with regards to heavy metal uptake from groundwater and other sources of drinking water found at or near DOE facilities were also tested. The nanomaterial-treated filters are advantageous because they serve as inactive supports that allow for efficient flow of the contaminated water and can be easily replaced after heavy metal uptake. They are also comparable to nanomaterials free in solution with regards to the effectiveness of remediation of drinking water.

1. Introduction

The industrial revolution and the advent of new innovations in fields such as medicine, engineering, and manufacturing have led to outstanding technologies that improved the standard of living and the life expectancy of our society. One of the drawbacks associated with these advancements is the potential release of contaminants and byproducts into the environment. The adverse effect of heavy metals and radionuclides on the environment have been recognized by the scientific community. While numerous strategies have been developed for decades^{1,2} new, cost effective, and efficient technologies are still being developed and implemented.

In recent years, there has been a growing interest in the fields of nanomaterials and nanotechnology.^{3,4,6,7} The first nanomaterial, buckminsterfullerene, was discovered in 1985 by Richard Smalley and Bob Curl. This discovery influenced scientists to consider the world at an atomic level.³ Since then, a large variety of novel nanomaterials have been produced and developed, including metallic, metallic oxide, polymers, quantum dots, among many others.³⁻⁷ In the last decade, these nanomaterials have been applied to the medical field, computer engineering, enhancement of instrumental analysis, material development, and environmental remediation^{3,4}. Due to the unique properties of nanomaterials in terms of reactivity, size to surface area ratio, optical and magnetic properties, and tunability³, they are prime candidates for the uptake of heavy metals from the environment.

There have been multiple studies that focus on the use of nanoparticles for the uptake of heavy metals in the environment. For example, Dupont et al.⁵ demonstrated the ability of EDTA-functionalized magnetic, Fe_3O_4 , and nonmagnetic, SiO_2 and TiO_2 , nanoparticles to selectively uptake earth metals from aqueous solutions. Recently, Warner et al.⁶ showed the ability of nanoparticles functionalized with five different ligands to serve as sorption agents for lead, mercury, copper, silver, cadmium, and cobalt. It was reported by Ojemaye et al.⁷ that nanoparticles functionalized with thiols, carboxylic acids, silanes, or nitrogen containing ligands are most efficient in the uptake of heavy metals due to the functional groups ability to bond with the heavy metal ions. All these techniques are effective at adsorbing heavy metals onto their surface. However, these strategies lack the capability of being practically implemented for widespread water remediation as fabrication of nanomaterials in large quantities is still limited. Moreover, nanomaterials' impact on the environment is currently unknown. Recent studies show that AuNPs stabilized with labile ligands (e.g., citrate or CTAB) aggregate irreversibly in groundwater, potentially reducing their environmental mobility. As a result, AuNPs movement through different ecosystem compartments might be better considered as the movement of large heteroaggregate species, rather than as individual nanoparticles.⁸ However, this limits the AuNPs surface area available for contaminant uptake and potentially affects their unique properties.

Although nanoparticles are viable options for environmental remediation, it is important to develop simple, yet controllable, methods for water clean-up that can be easily retrieved upon the capture of contaminants. Therefore, it is not practical to simply release free nanoparticles into water streams because it would be difficult to monitor individual particles and evaluate the remediation processes' efficiency. Magnetic nanoparticles that can be retrieved using magnets represent one possible solution to this problem. However, the magnetic properties of magnetic nanoparticles have been found to decrease in potency in wastewater, especially those that have been modified with ligands.⁷ Another viable alternative is the development of supported nanoparticles that can be used as efficient filters for contaminated water resources.⁹ This has the dual benefit of preventing nanoparticles from contaminating the environment and facilitating easier tracking and control of both nanoparticles and the heavy metal uptake on nanoparticles. Murph, et al.⁹ described recently a technique for the uptake of zinc vapors using nanoparticles attached to stainless steel filters. This technology is an environmentally safe and effective method for the remediation of heavy metals and radionuclides that is easily deployable and could be implemented in the field on contaminated waters.

This report describes the synthesis of nanoparticles on stainless steel wool filters that have been functionalized with an active ligand specifically designed to uptake heavy metals. Stainless steel is nonreactive and resistant to rusting, which makes it especially attractive for heavy metal uptake in an aqueous environment. Nanoparticles free in solution were also synthesized for a comparison of uptake efficiency.

2. Materials and Instrumentation

Chloroauric acid (HAuCl_4), sodium citrate (>99%), and L-cysteine (97%) were purchased from *Sigma Aldrich*. Zinc acetate and copper (II) nitrate hemi(pentahydrate) were purchased from *Sigma Aldrich* and used as sources for Zn^{2+} and Cu^{2+} ions, respectively. All aqueous solutions were prepared in deionized water. Stainless steel wool (Type 316L SSF) was used for the filters. All mass measurements were made with a *Metler Toledo* XPE105 balance. A *Fischer Scientific* accuSpin Micro17R was used for centrifuging the gold nanoparticles. A *TECS USA* MCS PDA with LS UV-Vis was used to evaluate nanoparticle's optical properties. The Zeta sizer and Zeta potential of the nanoparticles were obtained using a *Brookhaven Instruments* DLS NanoBrook Omni (110-240 V) manufactured in 2014. A *Hitachi* SU8200 Scanning Electron Microscope coupled with EDS was used for evaluating nanomaterials morphologies and compositions.

3. Experimental

3.1 Gold Nanoparticles Prepared in Solution

All glassware used in the following protocols was cleaned with Aqua Regia and then rinsed with deionized water. A sodium citrate solution (1%, 1 mL) was quickly added to a boiling solution of HAuCl_4 (2.5×10^{-7} M) under vigorous stirring. The solution was boiled for 10 minutes and then allowed to cool off. The appearance of a red color indicated the formation of the nanoparticles. The nanoparticles solution (1 mL aliquots) was then purified by centrifugation for 7 minutes at 10,000 rpm and redispersion in DI water. The AuNPs were then re-dispersed in 1 mL of deionized water.

3.2 Gold Nanoparticles Prepared on Stainless Steel Wool Filters

A sodium citrate solution (1%, 1mL) was quickly added to a boiling solution of HAuCl_4 (2.5×10^{-7} M) under vigorous stirring that contained a 1.5 cm^2 stainless steel wool filter in the flask. The solution was boiled for 10 minutes and allowed to cool off at room temperature (RT). The appearance of a purple - red - color indicated the formation of the nanoparticles. The nanoparticle treated filter was removed from the solution and rinsed with deionized water through three-step washing. It was subsequently transferred to a petri dish to dry for further use.

3.3 *Gold Nanoparticles Surface Functionalization*

The gold nanoparticles, both in solution and on the stainless-steel wool filters, were functionalized with L-cysteine. 100 μ L aliquots of L-cysteine (10 mM) was added to the 1 mL AuNP solution and incubated with stirring for 2 hours at RT. The functionalization of the AuNPs on SSW filters was done in the same manner in a 50-mL falcon tube. The solution was incubated for set time intervals (2 hours, 6 hours, and 24 hours) without stirring at room temperature. The functionalization of AuNPs with citrate occurs during their synthesis, as sodium citrate acts as the reducing agent in the reaction.

3.4 *Heavy Metal Uptake of Gold Nanoparticles*

The L-cysteine functionalized AuNPs and citrate-capped AuNPs in solution (1mL aliquots) were incubated while rotating at room temperature in a Zn^{2+} (1 mM) solution at different concentrations (0.05 mM, 0.1 mM, and 0.12 mM). The functionalized AuNPs on SSW filters were incubated without stirring at room temperature in a Zn^{2+} solution (1 mL) and 10 mL of deionized water with a 10:1 solution to heavy metal ratio. For comparison and testing of the selectivity of L-cysteine and citrate, the functionalized AuNPs, in solution and on SSW filters, were also incubated in the same manner with a Cu^{2+} (1 mM) solution.

4. Results and Discussion

4.1 *Synthesis and Characterization of Gold Nanoparticles in Solution and on Stainless Steel Wool*

Gold nanospheres were prepared in solution through a wet chemical approach using sodium citrate as a reducing and capping agent. The solution turned a ruby red color, which is indicative of gold nanospheres³. The SEM images confirmed the spherical shape of the AuNPs of approximately 21 ± 1 nm in diameter (figure 01). The AuNPs in solution were highly monodisperse in size and shape. The hydrodynamic radius of the nanoparticles investigated by the zeta sizer, in their aqueous environment, was 24 ± 0.1 nm, which is in agreement with the dimensions obtained by SEM on dried AuNPs. UV-Vis spectroscopy was employed to evaluate the AuNPs optical properties. The results show the presence of a sharp, single peak at 524 nm (figure 02) which is indicative of monodisperse and spherical AuNPs.

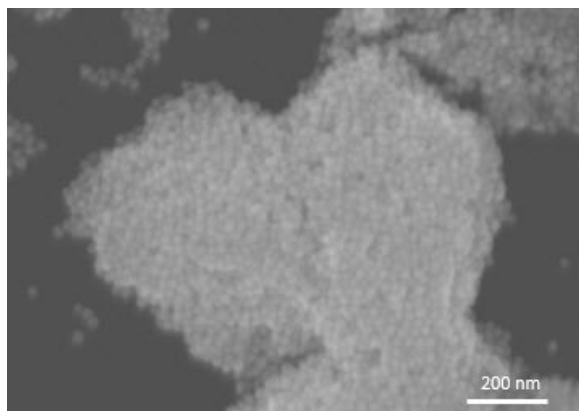


Figure 01: SEM image of 21 nm AuNPs prepared in solution.

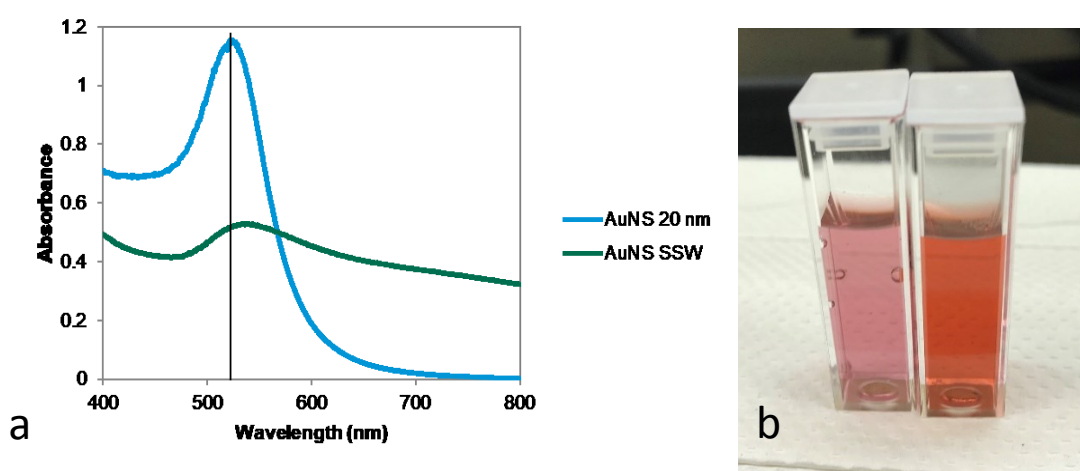
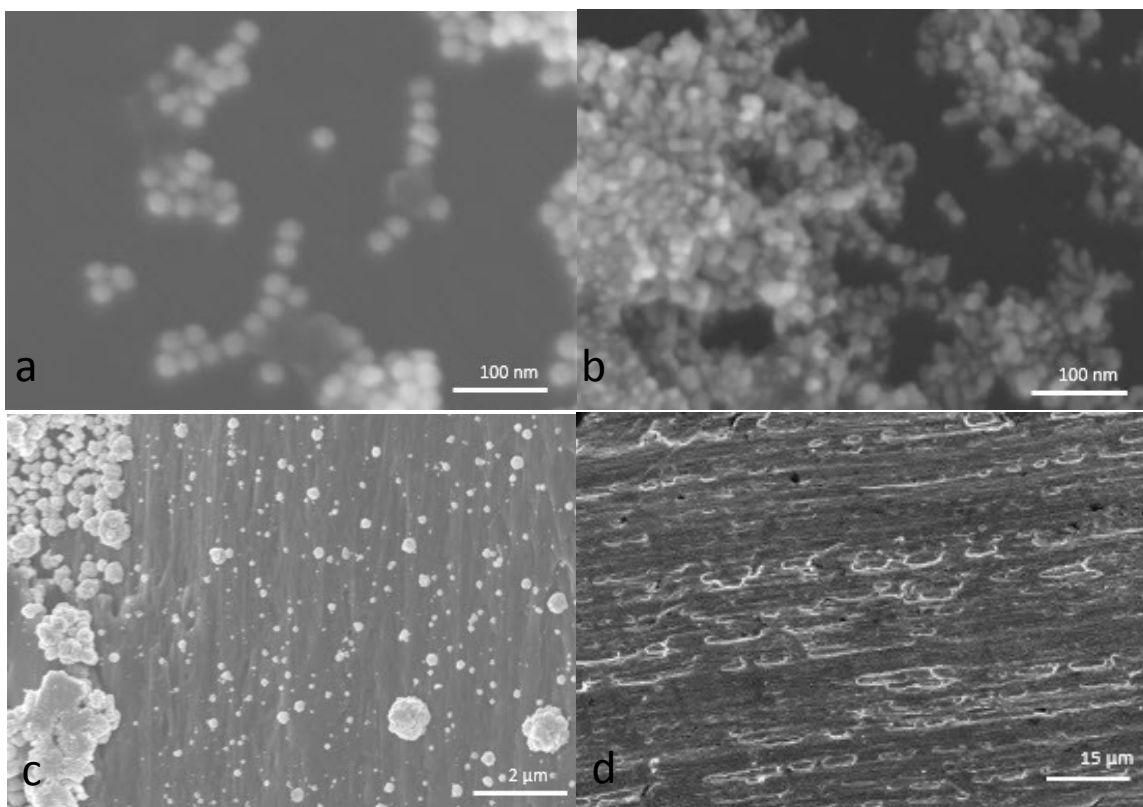


Figure 02: **a.** UV-Vis spectra for AuNPs in solution (blue) and on SSW filters (green), and **b.** noticeable color difference between the AuNPs on SSW solution (left, purple) and AuNPs free in solution (right, red).

The optical properties of AuNPs prepared on a SSW differ slightly when compared with the AuNPs in solution. The UV-Vis spectra of these AuNPs show a plasmon band peak at 533 nm. The NPs solution's color was a purple-reddish color (figure 02b). The plasmon band peak is broad indicating the presence of larger size nanoparticle and/or polydisperse nanoparticles. The SEM analysis supports the UV-Vis results, showing that the nanoparticles were polydisperse in size and shape with an average 25 ± 5 nm in diameter (figure 03). However, three different size populations were recorded, from 9.8 to 43 nm. Some AuNP clusters were produced on SSW. We also found that AuNPs formed on SSW (purplish-reddish AuNPs) were different in size from both those present in the solution or prepared in the absence of SSW supports free in solution (red AuNPs). The AuNPs produced on the SSW filters were, on average, 13 ± 1 nm in diameter. This is smaller than the 21 ± 1 nm diameter average of red AuNPs free in solution or 25 ± 5 nm average of purplish-reddish AuNPs. We suggest that the grooves and roughness of the SSW surface blocked and hindered the growth of larger AuNPs (figure 03d). The grooves had a diameter range

of 8 nm to 45 nm with an average of 26 nm. A comparison of the nanoparticle sizes is depicted in figure 04. This demonstrates that small changes in the environment, e.g. presence/absence of SSW in the reaction pot, leads to significant changes in the AuNPs morphologies³. ZetaSizer analysis was also conducted and showed an effective diameter of approximately double (52 ± 0.4 nm) for the nanoparticles remaining in the AuNP-SSW solution and not on the SSW itself.



*Figure 03: SEM images of **a.** 21 nm AuNPs free in solution, **b.** 25 nm AuNPs in the SSW supernatant, **c.** 13 nm AuNPs on SSW, and **d.** SEM images of stainless-steel wool control.*

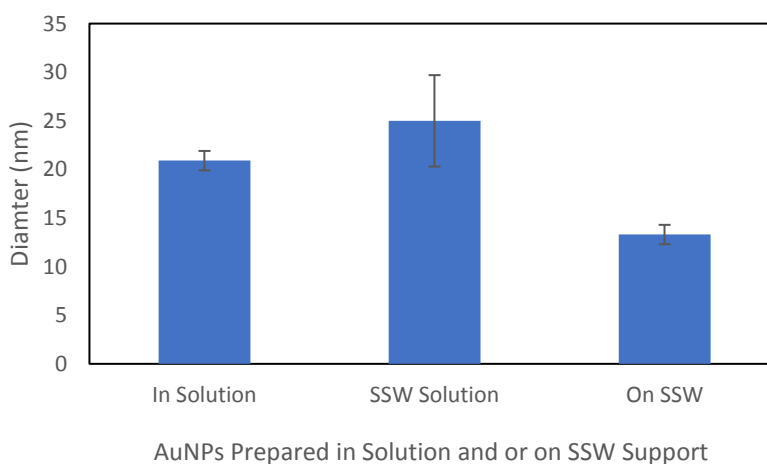


Figure 04: Comparison of AuNP particle size.

4.2 AuNP Surface Functionalization

Two different ligands, citrate and L-cysteine, were used for surface functionalization and testing. Both ligands have carboxylic acid groups that could be used for heavy metal uptake.¹⁰ Sodium citrate was used during AuNPs preparation and served as both reducing and capping agent. The selectivity and sensitivity of L-cysteine as a ligand that augments the ability of gold nanoparticles to uptake heavy metals has previously been reported.¹¹ L-cysteine is a multifunctional linker that binds to the AuNPs surface via the thiol bond and/or amino group.¹² The carboxylic acid group present at the other end serves as a “binding” agent for heavy metal uptake. At a pH of greater than 5.5, the carboxylic functionality is deprotonated, rendering a negative surface charge that can bind with positive heavy metal ions¹². The pH of the L-cysteine capped AuNP solution in this study was between 5.6 and 6.0.

The AuNPs surface functionalization with L-cysteine was monitored via UV-Vis spectroscopy; a red shift of the plasmon band of the gold nanoparticles was recorded from 524 nm to 526 nm upon attachment. The zeta potential of AuNPs was evaluated before and after surface functionalization. It was found that the original surface charge of the AuNPs of -39 mV became slightly more positive, -35 mV, upon surface engineering. The original negative charge is due to the citrate¹⁰, with the L-cysteine only marginally affecting the overall surface charge. The surface charge remaining negative is instrumental in cation uptake. These are indicators of successful surface functionalization. Information is summarized in table 01. The same procedure, including the concentration of L-cysteine was used for incubation with the AuNP SSW filters.

Table 01: Comparison of Zeta potentials, hydrodynamic radii, and plasmon bands for AuNPs in solution and ligand-modified.

Characteristics	AuNPs	AuNPs + Ligand
Zeta Potential	-39 mV	-35 mV
Zeta Size	24 nm	26 nm
Gold Plasmon Band	524 nm	526 nm

4.3 Heavy Metal Uptake in Solution

4.3.1 L-Cysteine Capped AuNPs

The unique optical properties of AuNPs in the visible region of the spectrum make them suitable for use as colorimetric sensors.¹⁴ The coupling of plasmon resonances of AuNPs that are within 1 diameter length apart upon the addition of analytes can be exploited as a colorimetric sensing technology. The original ruby-red color of the ligand capped AuNPs in solution turned blue upon addition of zinc ions. Moreover, as the concentration of Zn^{2+} increases, significant color changes can be observed with the naked eye; color changes from red to increasingly darker

shades of purple were observed (figure 05). Small color changes in AuNPs optical properties allow for a rapid and qualitative detection of heavy metal detection of Zn^{2+} on the ligand-modified AuNPs.

The optical properties of the colorimetric sensor were easily monitored via UV-Vis spectroscopy. The AuNPs plasmon band peak gradually red shifted from 524 nm to 689 nm as the Zn^{2+} concentration increased (figure 06). The gold plasmon band also became broader and less intense, which indicates that the Zn^{2+} was captured on the AuNPs surface and causing them to agglomerate. This is also supported by the color change shown by the nanoparticles as colorimeter sensors, from red to purple to dark blue. The hydrodynamic radius of the Au NPs increased from 27 nm when no Zn^{2+} was present to 236 nm with the highest Zn^{2+} concentration of 0.12 mM (table 02). The surface charge of the nanoparticles became more positive after the addition of the Zn^{2+} , which is also an indicator that the Zn^{2+} interacted with the surface of the nanoparticles. A similar behavior was observed for Cu^{2+} (table 03).

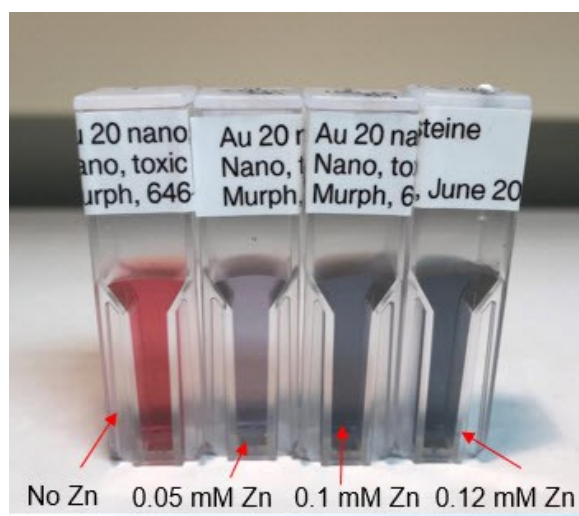


Figure 05: AuNPs as colorimetric sensors in the presence of Zn^{2+} .

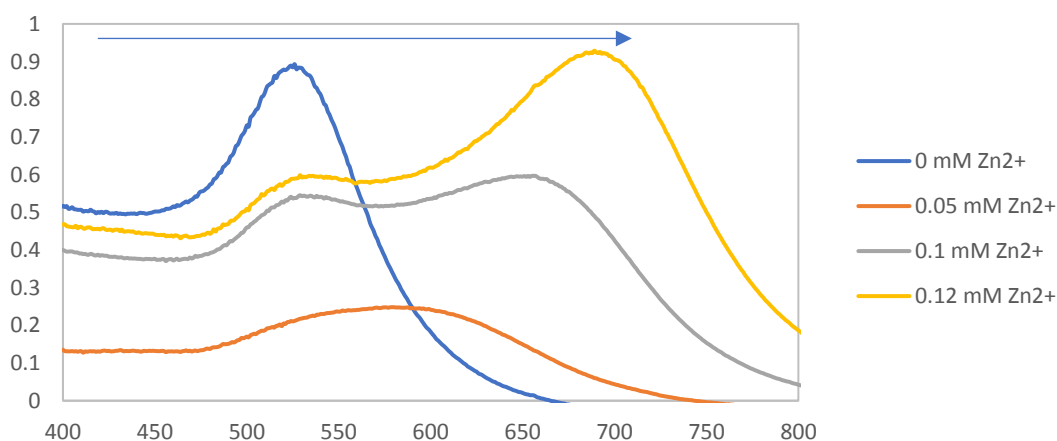


Figure 06: UV-Vis spectra for L-cysteine modified AuNPs with different Zn^{2+} concentrations.

Table 02: Comparison of zeta potentials and hydrodynamic radii with respect to concentration of zinc ions added.

Zinc Ion Concentration (mM)	Zeta Potential (mV)	Zeta Size (nm)
0	-35	27
0.05	-22	68
0.1	3.4	84
0.12	1.9	236

Table 03: Comparison of zeta potentials and hydrodynamic radii with respect to concentration of copper ions added.

Copper Ion Concentration (mM)	Zeta Potential (mV)	Zeta Size (nm)
0	-35	27
0.05	-22	151
0.1	-10	173
0.2	-0.8	87

4.3.2 Citrate Capped AuNPs

An additional heavy metal, Cu^{2+} , was also tested to investigate potential ligand and/ or AuNPs selectivity. Two different ligands were tested, L-cysteine and sodium citrate. However, upon incubation with Cu^{2+} ions, from copper nitrate, the L-cysteine capped AuNPs crashed. We found out that the initial pH of the L-cysteine capped AuNPs aqueous solution decreased from pH = 5.6 to pH = 3.9 upon addition of Cu^{2+} ions, which negatively impacted the AuNPs stability. However, the citrate capped AuNPs were not affected by the addition of Cu^{2+} ions as their properties did not change.

Upon testing, we found that the citrate capped AuNPs can serve as sorbent materials for both Cu^{2+} and Zn^{2+} . Citrate binds with copper through a chelation bond, in which electron-donating from citrate to copper makes the central metal ion more electron rich.¹⁵ The negatively charged oxygen atom of citrate's carboxylate groups establishes a coordination interaction with the Cu^{2+} ion.¹⁵ The affinity of citrate for Zn^{2+} has also been reported by others.¹⁶

Citrate had a greater sensitivity towards the Cu^{2+} , which supports previous studies¹⁴, as the colorimetric sensor demonstrated a visible color change at a lower concentration of Cu^{2+} than Zn^{2+} (figure 07). The UV-Vis spectra were used to monitor both ions' uptake. A concentration of 0.2 mM or lower Zn^{2+} with citrate had no impact on the plasmon band position. A concentration of 0.3 mM Zn^{2+} causes a significant plasmon band shift from 524 nm to 676 nm. Surprisingly, a different behavior was recorded when L-cysteine capped AuNPs were incubated with Zn^{2+} . A small red shift from 524 nm to 544 nm is observed at the lowest added concentration of Zn^{2+} , 0.05 mM, and shifts further to 663 nm at 0.1 mM. The plasmon band position remains in the same area as the position of the 0.1 mM plasmon band, even upon the addition of more Zn^{2+} . A concentration of 0.1 mM Cu^{2+} with citrate causes a very small red shift of only 5 nm from 524 nm to 529 nm and continues to increase steadily as the concentration increases (figure 08). This demonstrates that citrate capped AuNPs has a greater sensitivity for Cu^{2+} than Zn^{2+} , making them more suitable as a sensor for Cu^{2+} .

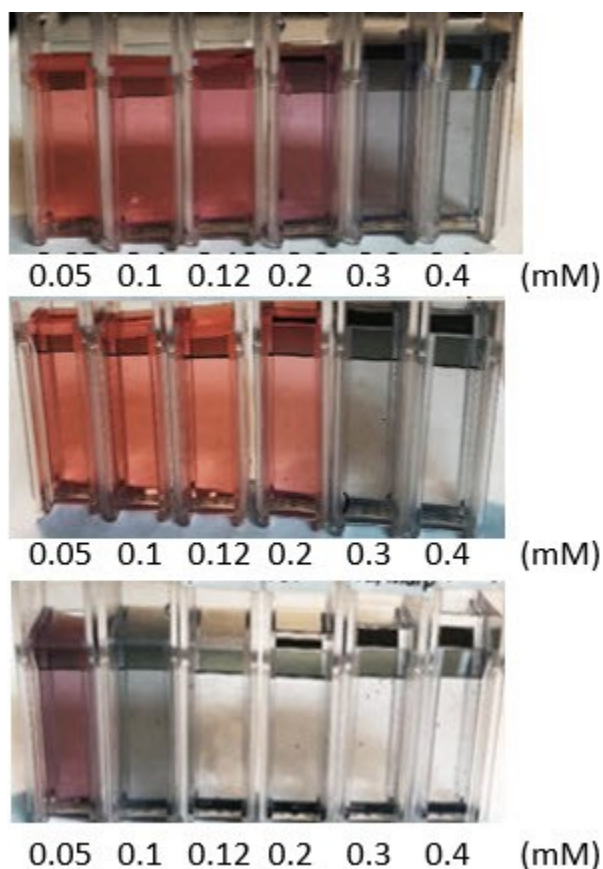


Figure 07: Comparison between colorimetric sensor for Zn^{2+} with citrate and AuNPs (top), Zn^{2+} with L-cysteine and AuNPs (middle), and Cu^{2+} with citrate and AuNPs (bottom). The concentration of heavy metal ions increases from left to right.

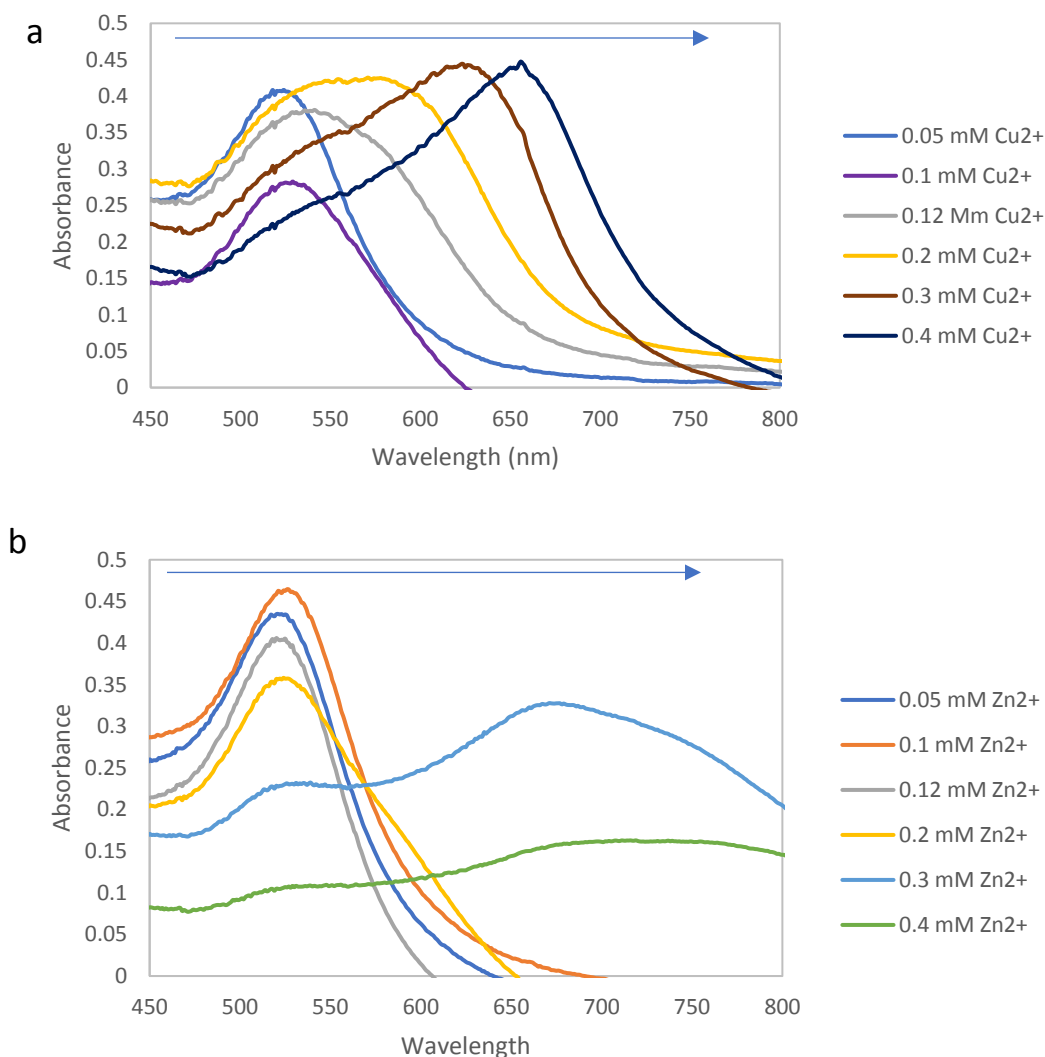


Figure 08: UV-Vis spectra for AuNPs with different Cu²⁺ (**a**) and Zn²⁺ (**b**) concentrations and citrate as the ligand.

4.4 Heavy Metal Uptake on AuNP treated SSW Filters

Au nanoparticles treated SSW were also incubated with heavy metal ions and evaluated for their uptake. A visual comparison of the SSW filters prior to modification and after heavy metal ions incubation is seen in figure 09, and the color differences are suggestive of an interaction occurring. SEM and EDS were used to evaluate heavy metal uptake. The presence of Zn²⁺ was detected by EDS (figure 10); while this is a semi-quantitative study, the preliminary data suggests a 5:1 ratio of Au: Zn²⁺. The presence of the zinc ions shows that L-cysteine capped AuNP-treated SSW filters are effective at the uptake of heavy metals.



Figure 09: (From left to right) Control SSW, AuNP-treated SSW, L-cysteine modified AuNP-treated SSW with Zn^{2+} after 24 hours incubation.

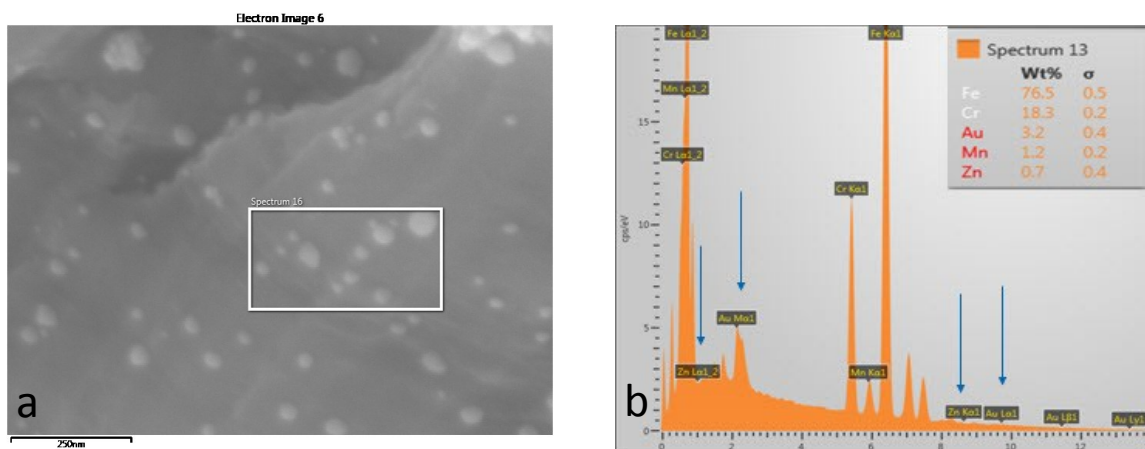


Figure 10: **a.** EDS image of L-cysteine modified AuNPs on SSW incubated for 24 hours with Zn^{2+} , and **b.** EDS elemental composition spectrum showing peaks for Zn^{2+} and gold for the L-cysteine modified AuNPs on SSW incubated for 24 hours with Zn^{2+} .

5. Conclusions

We described the successful synthesis and characterization of ligand-modified gold nanoparticles (AuNPs) in solution and grown on stainless steel wool filters. Two different sensing and remediation technologies were developed including (a) a heavy metal colorimetric sensing technology and (b) a citrate AuNP-treated filtering technology for environmental remediation applications. Citrate capped AuNPs in solution show a greater heavy metal loading capacity than L-cysteine functionalized AuNPs. This suggests that they could be used for remediation applications. It was also found that the citrate-capped AuNPs have a greater sensitivity for Cu^{2+} than Zn^{2+} . L-cysteine capped AuNPs are more sensitive towards Zn^{2+} making them valuable for sensing applications. AuNP SSW filters exhibit different characteristics than AuNPs in solution (size, shape), and are efficient at the uptake of heavy metal ions.

6. Acknowledgements

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