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DEVELOPMENT OF A NOVEL CARBON-BASED SENSOR FOR THE DETECTION OF DISSOLVED METAL IONS USING *LEUCOBRYUM GLAUCUM*

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Abstract

Access to clean drinking water remains a serious issue globally. This crisis is a substantial issue in first-world countries, just as it is in developing nations. Inhabitants of Oregon are currently subject to water pollutants present in many community wells and water systems, representing a widespread public health issue. Carbon Quantum Dots (CQDs) have extensive applications that have shown promising results as they are being used for in vivo optical imaging studies due to their florescent properties. Their affordable and rapid synthesis makes these materials ideal aqueous candidates to serve as metal ion detectors. This study synthesized CQDs from *Leucobryum glaucum* and tested their ability as fluorescent sensors of dissolved metal ions, which may be applied to combatting the Oregon water crisis.

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Introduction

Access to clean drinking water is an issue that affects people around the globe. [1]An estimated two thirds of the world's population - four billion people - experience a severe scarcity in water access for a minimum of thirty days each year. [2] They are forced to find other water sources that may not always be the best quality, creating potential exposure to water borne pathogens, dissolved metal ions, runoff and the risk of contracting illnesses.[1] The global water demand is expected to rise 55%, while currently a rough approximation of 25% of large cities are experiencing some levels of water stress.[1] The aforementioned issues can also be present in much more developed nations located in parts of first-world and developing countries. Even countries that appear to have adequate water resources still do not have enough supplies for everyone. Global water sustainability will not be reached without ensuring the availability of safe water for all who need it.

Many of these issues can occur as a result of collapsed infrastructure, distribution systems, contamination, and poor management of water resources.[2] As the water shortage worsens, many areas of society can be affected such as individual communities, commerce, industries, and agricultural systems facing the risk of impact. Recently, the state of Oregon has experienced several public health concerns. There have been 11 water related insecurity interventions where at least two water borne disease outbreaks have affected individuals that use public water systems. In June of 2011, Oregon reported 119 cases of cryptosporidium which resulted in two hospitalizations. As a result of these findings, they garnered and raised concern for the citizens of Oregon. They also highlight a link between a growing number of hospitalizations from a lack of access to clean and safe drinking water in first world countries.[3]

This recent surge caused the Oregon Health Authority (OHA) to administer the Safe Drinking Water Act (SDWA), which requires public water systems to report their annual water quality to consumers. Roughly 80% of Oregonians access their drinking water from public water systems, much of which have been reported to have average quality at best (Figure 1)[9]. Further complicating the issue is that many of the people in Oregon use private domestic wells as their primary source, leaving the testing of water quality to the owner of the well. [3] Counties such as Crooks, Deschutes, Grant, Harney, Jackson, Jefferson, etc. have requested declarations for drought aid from the local commissioner in order to access quality drinking water.[3] The impacts of the Oregon water crisis have not diminished and are impacting the health of Oregonians daily. These issues warrant investigation into the need for interventions regarding water quality for the people of Oregon.[4]

Recently, Carbon Quantum Dots (CQDs) have been a rapidly emerging and expanding field of study.[4] Among other properties, CQDs possess fluorescent properties which can be tuned. The fascinating properties of these materials may contribute to their expanding potential applications in a variety of areas including conventional semiconductors, catalysts, and surface passivation qualities that further adds to their physiochemical properties. Of particular note, some current uses of these materials are emerging in drug delivery, electronic media, and as aqueous metal detectors.[5] The simple synthetic routes to produce these nanoparticles from non-toxic and environmentally friendly materials help reduce the overall cost of production. This has further increased their potential in many fields of research.[4] Ultimately, nearly any carbon-rich source can be leveraged as the starting material for synthesis,

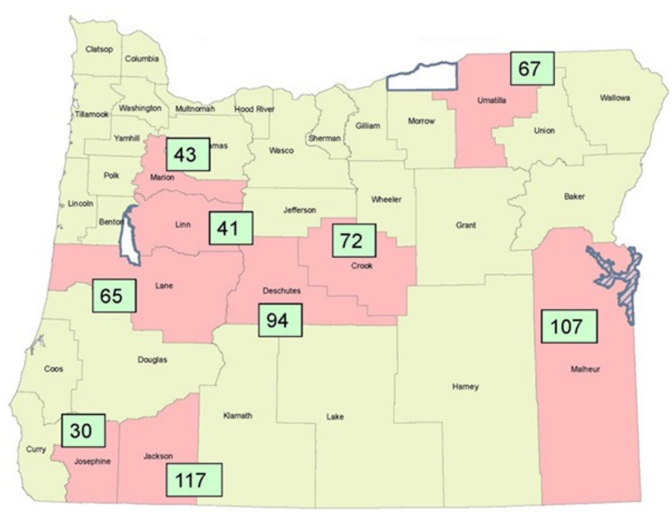

Figure 1. Oregon Counties with highest number of well systems reported with contaminated nitrate levels above 7mg/L.[9]

allowing researchers to make use of abundant, sustainable, and accessible sources to create samples for testing applications.

Interestingly, forest moss (*Leucobryum glaucum)* has been a major, non-timber, white product for a number of years in Oregon. (Figure 2)[6,11] Many regions of Oregon are dominated by mixed forests while epiphytic bryophytes (mosses) thrive in the coastal ranges.[7] A number of studies of these plants are already being carried out to determine ecosystem difference and evaluate the recovery rates of these mosses.[8] Ultimately, with the abundance of *Leucobryum glaucum* in Oregon, this work will attempt to use this readily available carbon-based material to produce CQDs to test for the presence of dissolved metal ions. If successful, this work may serve to supply additional water testing methods for the inhabitants of Oregon.

Experimental Methods

Salts of $CuCl_2$, $CoCl_2$, $NiCl_2$, and $ZnCl_2$ were obtained from Sigma Aldrich and dissolved in distilled H_2O to produce 100 mM stock solutions which were used and diluted as needed without further purification. Samples of *Leucobryum glaucum* were collected from wooded areas of Stevenson University's North Campus, found of the bark of the areas native tree species. The sample was stored in a ventilated storage container until experimentation. The preparation of CQDs was accomplished through the hydrothermal treatment of the white moss samples according to the established procedures by Liu et al.[11] Their rigorous validation techniques for quantum dots produced by this method provides a reliable precedent and confidence in the identity of the samples created. The specific details of this study are as follows: In a Teflon-lined autoclave, 2 g of white moss was suspended in 20 mL of distilled H_2O. This mixture was then heated at 180° C for 3 hr. The resulting mixture was centrifuged at 12000 rpm for 10 minutes and the supernatant was collected and used without further purification.

Metal ion detection tests were carried out by adding 125 µL of the CQD solutions to samples with a final concentration of 50 µM, $CuCl_2$, $CoCl_2$, $NiCl_2$, and $ZnCl_2$ ions. For initial investigations into the suitability of these samples as aqueous sensors, this concentration (50 µM) has been studied before[11] and will serve as the ion concentration for these trials. The comparative control was prepared in the same manner, simply replacing metal solutions with distilled water. Fluorescence data was collected using a fluorimeter (model: Jaz, manufacturer: OceanWay) with an excitation wavelength of 385 nm, and emission wavelengths were collected at 495.73 nm. These measurements were recorded at 10 min of samples incubation, and again for the same samples after a seven-day incubation period. All samples were performed in duplicate.

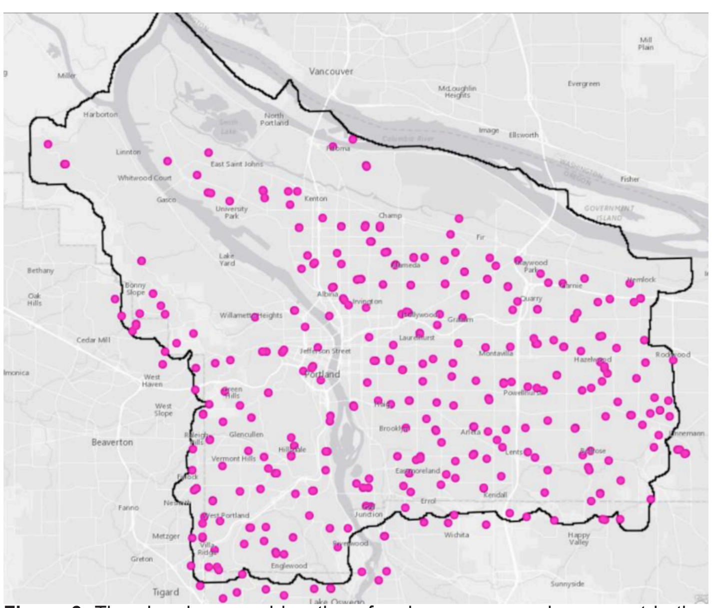

Figure 2. The abundance and location of various moss species present in the Portland Oregon region.[6]

Results and Discussion

Full emission spectra were collected for each sample, with a representative graph provided in Figure 3. From these spectra, a consistent maximum was observed at 495.73 nm and therefore was used to record the fluorescence intensity data throughout this study. Therefore, intensity readings at 495.727 nm collected and analyzed throughout this study.

The results of the seven-day incubation period of the CQDs are displayed in Figure 4. For all tests completed in this study, duplicates of all trials were performed and, due to the general consistency of the results throughout (as evidenced in Figure 4), average intensity values were calculated and will be discussed for all other tests. After seven days it was observed that both the Zn^{2+} and Ni^{2+} samples increased in fluorescence intensity noticeably, on average, compared to the controls. Although the Ni^{2+} samples displayed some deviation from each other, the average value of the emitted intensity still displays a significant difference from the controls. The increase of fluorescence of these metals represents a qualitative visual change, and therefore have potential to serve as a detector of the presence of Zn^{2+} and Ni^{2+} in water. Conversely, both Co^{2+} and Cu^{2+} samples were observed to display a noticeable decrease

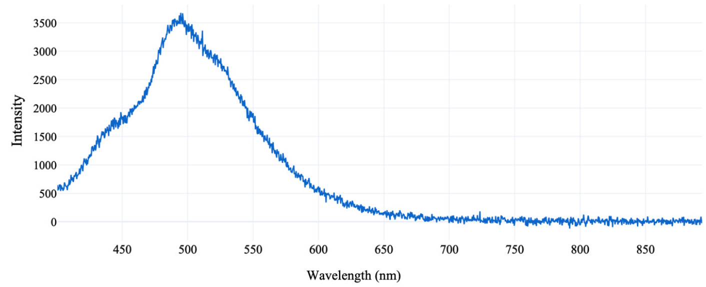

Figure 3. Representative fluorescence spectra demonstrating the raw data collected throughout this study.

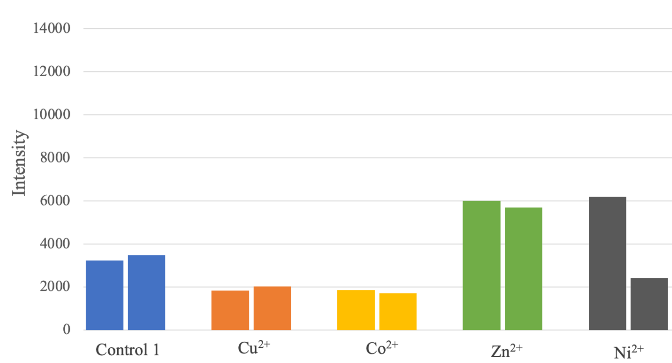

Figure 4. Fluorescence intensity data collected after seven days of incubation.

in fluorescence intensity, compared to the controls. Although this trend is opposite to the other two metal ion samples, the clearly observed difference, when compared to the controls, still indicates that these CQDs are able to interact with the dissolved ions in a way that can be detected by this simple process. These opposing behaviors are still consistent with the literature, where researchers have observed nanoparticles interacting with dissolved species and, in some cases, yield a reduction of the emitted fluorescence, while other times this intensity seems to be enhanced.

To determine if these CQD nanoparticles might serve as a more rapid metal ion detector, an incubation time of just ten minutes was performed and the fluorescence intensities were collected.[11] It can be seen in Figure 5 that the average fluorescence intensities for three of the species displayed the same general trend as previously described for the longer incubation trials, while only one species displayed a different behavior. Similar to the seven-day trial, both the Cu^{2+} and the Co^{2+} samples yielded an immediate and significant decrease in fluorescence intensity compared to the control, while the Zn^{2+} samples once again displayed a noticeable increase. The Ni^{2+} samples, however, were observed to produce a lowered intensity compared to the control, unlike the opposite results that were observed after seven days. Although the extent to which the fluorescence was affected was not as dramatic as the Cu^{2+} and Co^{2+} samples, it was still a significant enough change to warrant discussion here. To further investigate these differences, the two incubation periods were then directly compared.

The combined results shown in Figure 6 bear out the trends discussed earlier. When comparing shorter and longer incubation times, it is clear that the overall relationships remain fairly consistent. Both Cu^{2+} and Co^{2+} tests display significant decreases when compared to controls, while Zn^{2+} samples display noticeably higher fluorescence intensities at both incubation times. The only samples that warrant any hesitation are the Ni^{2+} trials, where shorter incubation times seemed to display an initial lowering of fluorescence intensity, while a longer incubation period seems to allow for a unique interaction to occur.

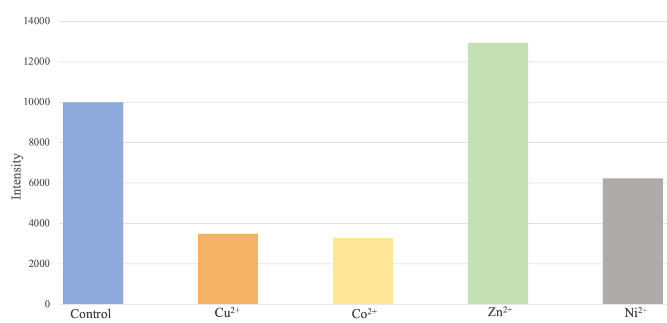

Figure 5. Average fluorescence intensities collected after ten-minute incubation.

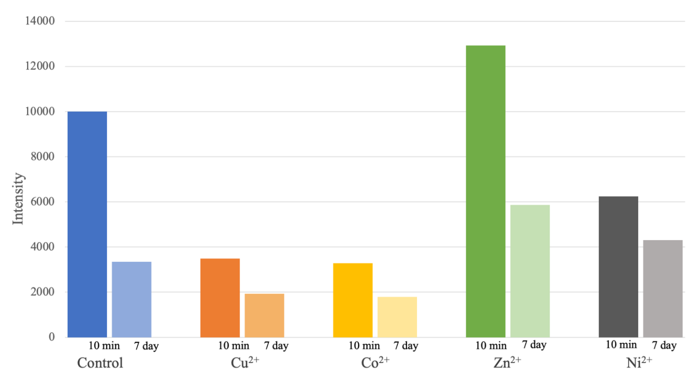

Figure 6. Average fluorescence intensities collected for 7-day tests compared to 10 minute tests

In general, percent change (as compared to the controls) may be the simplest method to analyze all the collected results, as well as help determine the overall efficacy of these nanoparticles, if they are to be used as aqueous ion sensors. Both the Cu^{2+} and the Co^{2+} samples were observed to yield fairly consistent average intensity reductions for both incubation times (46% and 54%, respectively). Additionally, the Zn^{2+} samples displayed increased signal intensities between 31% and 53%, after ten minutes and seven days respectively. While more testing would be necessary to confirm these results, it may be possible to use percent changes like these to not only make qualitative determinations about whether or not a dissolved metal ion is present, but perhaps also be able to identify which metal species it is based on these unique percentage ranges. Finally, although the Ni^{2+} samples were different from the controls at both incubation times, the fact that the behavior of that species showed an inversion of its results leads to a hesitation in making any definitive claims for it at this time. More work would need to be performed to better understand the specific interactions these CQDs seem to be having with dissolved Ni^{2+} before advocating for these nanoparticles to be used to broadly test for this specific ion. For further study, testing a combination of metals would allow for analysis of ion interactions with the CQDs with competing binding interaction. Additionally, controlling factors like pH in future work may add insight into how these complex mixtures may affect the fluorescent behaviors of these novel sensors. Together with the results from the current study, looking into the results of these follow up experiments may provide an even better understanding of the application of these samples as field metal ions detectors for the Oregon Water Crisis.

Taken together, this preliminary work has demonstrated that CQDs synthesized from *Leucobryum glaucum* may provide an accessible and affordable sensor for detecting the presence of several metal ions in drinking water sources, over a variety of testing timeframes.

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