

NOVEL ASSESSMENT OF WATER POTABILITY IN WEST AFRICA USING CARBON-BASED QUANTUM DOTS DERIVED FROM *S. DUCIFICUM*

Alyssa D. Reddy*^a, Anna K. Zadel*^b, Madison J. Parker*^a, Ashley V. Cook*^a, and Jeremy Burkett^{†a}

^aDepartment of Biochemistry and Chemistry, Stevenson University, Owings Mills, MD 21117

^bDepartment of Biological Sciences, Stevenson University, Owings Mills, MD 21117

Abstract

There is a water crisis in West Africa caused by contamination from heavy metal ions such as Co^{2+} , Cu^{2+} , and Ni^{2+} that affect vital irrigation and drinking water. Considering the need for rapid, accessible and affordable methods for detecting dissolved metal ions in the West African region, specifically Nigeria, *S. dulcificum* may be an effective source for the creation of carbon quantum dots to be used as aqueous metal-ion sensors. *S. dulcificum* underwent hydrothermalization to create carbon quantum dots, and these synthesized nanoparticles were used in metal ion-containing solutions to evaluate fluorescence quenching over ten minutes and seven days. There was a similar trend between the ten-minute and seven-day tests where the fluorescence intensity of the Cu^{2+} decreased by an average of 60% from the Control, Co^{2+} samples by 80%, and Ni^{2+} samples by 37%. Due to this comparable decrease in fluorescence, *S. dulcificum* carbon quantum dots are not only effective but are capable of working fast to produce detection results of copper, cobalt, and nickel metal ions.

[†]Corresponding author: jburkett2@stevenson.edu

*Undergraduate researchers and co-authors

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Introduction

In West Africa, there is a water crisis caused by heavy metal contamination that affects vital irrigation and drinking water. According to the Environmental Performance Index (EPI) for water quality, all ten of the lowest scoring countries are in this region (Figure 1)¹. In particular, Nigeria is one of the countries that experiences the highest levels of these toxic heavy metals in its water sources. Most notably, dissolved cobalt, copper, and nickel ions exist at high concentrations and can pose serious side effects on those who drink this contaminated water². These side effects can include memory loss, deafness, vertigo³, kidney damage, lung fibrosis, gastrointestinal issues, cirrhosis⁴, and contact dermatitis among others.⁵

The quality of water in Nigeria is critical due to its population's reliance on bodies of water for drinking, irrigation, and use in manufacturing yet the EPI determined that the quality score of Nigeria's water was 14.6 out of 100¹. Between 2000 and 2019, the average metal concentrations of Co^{2+} , Cu^{2+} , and Ni^{2+} ions, and other metals were dangerously high in all of these water sources². The highest contamination of copper was 4.90 mg/L in a river

in Kano measured in 2013 exceeding the World Health Organization (WHO) maximum recommendation for drinking water at 2.0 mg/L.^{2, 6} The highest concentration of cobalt was 1.90 mg/L found in the same river². This concentration is concerning since the measured value is three orders of magnitude higher than the recommended standard of reporting (0.001 mg/L)⁷. Nickel concentrations were found to be 6.78 mg/L in a different river in Ilorin in 2003 with the next leading concentration at 2.05 mg/L in the Benin river². Once again, these measured values far exceed WHO and the National Agency for Food and Drug Administration and Control for Nigeria (NAFDAC) standard (0.15mg/L). These high concentration ranges demonstrate a desperate need for rapid and accurate testing of drinking water sources. While several techniques currently exist, many of them are costly and inaccessible in regions such as these in West Africa.

Carbon quantum dots (CQD) are nano-scaled particles that are carbon-based substances produced through pressurized hydrothermalization⁸. Due to the size of these particles, carbon quantum dots can exhibit several molecular properties including fluorescence. The fluorescent behavior of carbon quantum dots can be affected by the presence of metal ions, which can result in a decrease of the fluorescent emission.^{9, 10} The change in emission is likely due to the binding of metal ions to the carbon quantum dots which results in a change of size. Fluorescence quenching is caused by metal ions accepting electrons from the carbon dots, which leads to the aforementioned decrease in intensity of emission⁹. This observable difference in fluorescence between samples that do and do not contain metal ions may allow for carbon quantum dots to be used as an effective sensor for drinking-water samples⁹⁻¹¹.

Previous research has shown that quantum dots can be produced from a wide variety of carbon sources.¹² Of particular note, *Synsepalum dulcificum* (*S. dulcificum*), which is native to West African countries such as Ghana, Togo, Benin and Nigeria, is an accessible and carbon-rich source that may prove to be a good starting material¹³. This African fruit, when tasted, allows sour foods to be perceived as sweet because of its taste-modifying properties, in

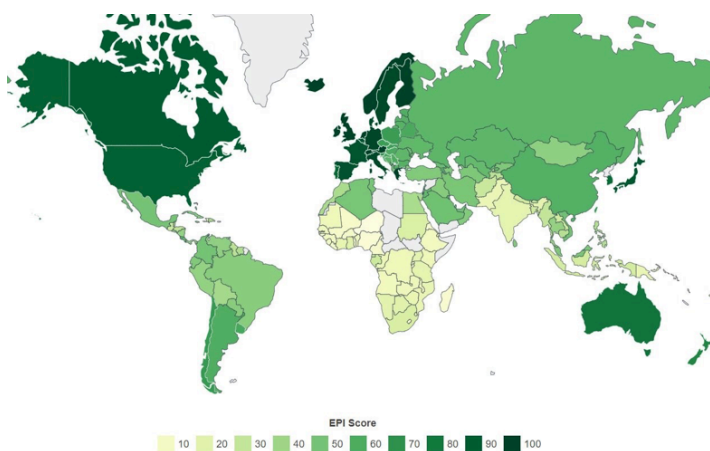


Figure 1. EPI of global water quality¹.

the form of a glycoprotein sweetener called miraculin.^{13,14} For this, the plant earns the common name of “Miracle Berry”. *S. dulcificum* also has a variety of medical uses such as treatment of diabetes, malaria, hyperthermia, tuberculosis, high cholesterol, and serves as a source for various pharmaceutical products and vitamin C and E¹³⁻¹⁵. Moreover, *S. dulcificum* has already been used as a catalyst in the phytosynthesis of silver nanoparticle (AgNPs)¹⁶. It is likely that this fruit can be effective in producing high concentrations of carbon quantum dots on its own because it contains various sugar compounds, such as nicotinic acid and β -sitosterol¹⁴. Considering the need for rapid, accessible and affordable methods for detecting dissolved metal ions in the western African region, *S. dulcificum* may be an effective source for the creation of carbon quantum dots to be used as aqueous metal-ion sensors.

Experimental Methods

Salts of CuCl_2 , CoCl_2 , ZnCl_2 , and NiCl_2 were purchased from Sigma Aldrich and used without further modification. Fluorescence readings were performed using a JAZ Ocean View fluorimeter. Samples were prepared by grinding freeze-dried *S. dulcificum* berries into powder. Three separate solutions were created with 0.5 g, 1.0 g and 1.4 g in 40 mL of water each and heated to 40° C, then stirred until mostly dissolved. Using a Teflon-lined steel autoclave, the solution at 200° C for three hours. The resulting solutions were then filtered and used without further modification.

Stock solutions of 110 mM metal ions were prepared with CuCl_2 , CoCl_2 , ZnCl_2 , and NiCl_2 salts. Samples were prepared to include a final concentration of 55 mM metal-ion and 15% of the concentrated CQD solution in PBS buffer¹². As CQD from *S. dulcificum* have not been synthesized nor tested previously, this higher concentration solution was used to explore feasibility of using CQDs from *S. dulcificum* with a various metals for preliminary results¹². Fluorescence measurements were collected in duplicate for control samples, Co^{2+} , Cu^{2+} , Zn^{2+} , and Ni^{2+} solutions for incubation times of ten minutes and seven days using an excitation wavelength of 385 nm with an emission wavelength of 496 nm.

Results

Carbon Quantum Dot Synthesis

The presence of carbon quantum dots was verified through fluorescence testing after hydrothermalization. All samples displayed a maximum emission peak at 496 nm when an excitation wavelength of 385 nm was used. Figure 2 demonstrates the full

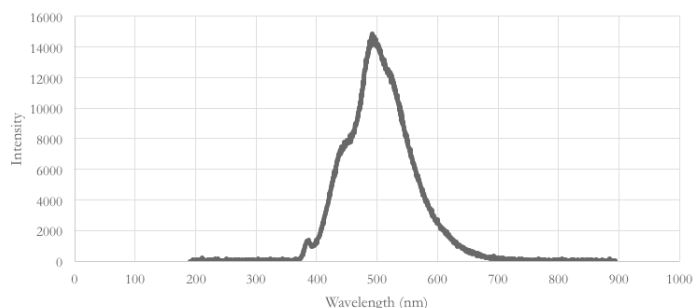


Figure 2. Sample spectra of fluorescence intensity scan using an excitation wavelength of 385 nm. Fluorescence intensity of 15% diluted sample of 1.4 g carbon quantum dot product, which shows a peak at 496 nm.

spectrum collected for each sample; however, since the maximum emission intensities have been isolated and displayed for all forthcoming samples to ease the discussion of the results (Figure 2). A serial dilution of the sample was conducted to determine optimal concentration of quantum dots for metal ion testing of 15% (Figure 3). This concentration was used as the optimal concentration throughout the rest of the experiments.

Metal Ion Testing

Fluorescence quenching from metal ions after ten minutes was observed, specifically with the Co^{2+} , Cu^{2+} and Ni^{2+} samples (Figure 4). With an average decrease of 62% in intensity, the Co^{2+} sample had a lower intensity than each of the Control samples. The most decrease was displayed in Cu^{2+} containing sample with an 88.5% decrease on average. With an average decrease of 30%, the Ni^{2+} sample was effective but did not have as much decrease as the samples that contained Co^{2+} and Cu^{2+} . There was a slight increase of 2.5% on average for the Zn^{2+} sample.

Due to the consistency shown by each sample, averages of the duplicates were calculated and will be displayed from this point on. The samples were allowed to incubate for seven days and were

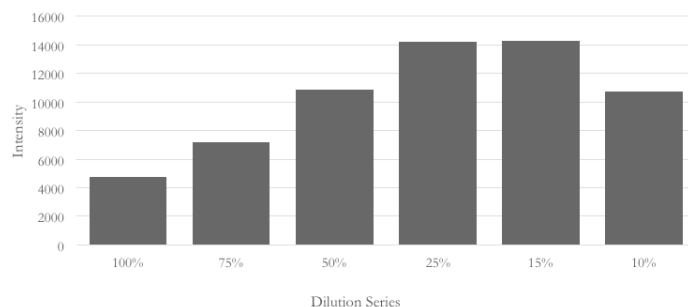


Figure 3. Fluorescence intensity of dilutions of 1.4 g carbon quantum dot samples recorded at 496 nm.

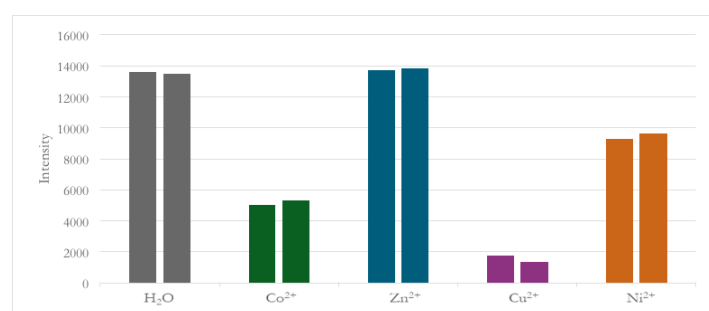


Figure 4. Fluorescence intensities of metal ion samples after ten minutes of incubation.

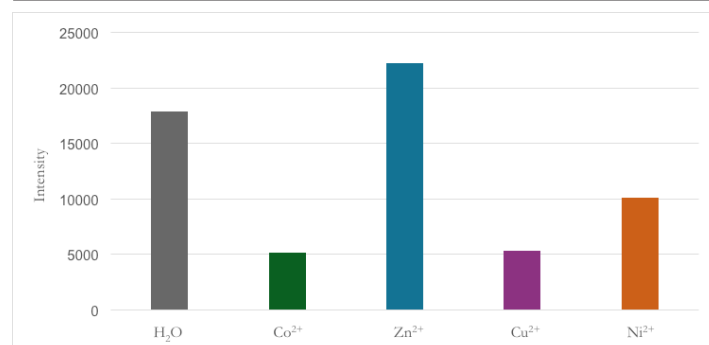


Figure 5. Average fluorescence intensities of metal ion samples after seven days of incubation

rescanned to determine fluorescence intensities (Figure 5). There was a significant decrease for the Co^{2+} sample of 59% in the intensity compared to the Control. Although the Co^{2+} sample intensity was low, the Cu^{2+} sample displayed the lowest intensity, just as it did in Figure 4, at a decrease of 70%. The Ni^{2+} containing sample still had a higher intensity compared to the Co^{2+} and Cu^{2+} samples but had a decrease of 43% of the intensity from the Control. While the Co^{2+} , Cu^{2+} , and Ni^{2+} samples all had a lower intensity compared to the Control, the Zn^{2+} sample on the other hand, had a significantly high intensity compared to the other metal ions with a 25% increase.

Overall, previous figures display that the fluorescence intensities of each metal ion-containing sample changed to some degree after seven days, but despite this change, the relationships of the fluorescence intensities for each sample when compared to each other or the Control remained the same. For instance, the percentage relationship of the Co^{2+} sample to the Control was a difference of 62% after and a difference of 59% after seven days of incubation. To this point, the overall relationship of Co^{2+} , Cu^{2+} , and Ni^{2+} samples to the Control is that these metal-ion-containing samples displayed fluorescence intensities lower than that of the Control, which qualifies the ability of the *S. dulcificum* carbon quantum dots to quench fluorescence in samples that contain these metal ions.

Although metal ions Co^{2+} , Cu^{2+} , and Ni^{2+} were shown to be detectable in water by the carbon quantum dots, the Ni^{2+} sample, of particular notice, exhibited a comparable intensity of fluorescence for both the ten-minute and seven-day tests (Figure 6), with a percent increase of only 7%. This relative stagnancy in fluorescence is amplified by the noticeable 24% increase in fluorescence intensity of the Control between the ten-minute and seven-day test, which lacked metal ions for detection. This unusual behavior exhibited by the Ni^{2+} sample raises a notable consideration that the carbon quantum dots synthesized through this research can be used in the rapid testing of water samples for metal ions of Nickel, alleviating the necessity of waiting seven days for more accurate detection results.

From this study, it is seen that the testing of water samples that contain Co^{2+} , Cu^{2+} , and Ni^{2+} would yield results that demonstrate a clear presence of these metal ions. However, the same result would not be yielded by a sample containing metal ions of Zinc, as the Zn^{2+} sample in this study displayed a trend of fluorescence intensity that was not only higher than that of the other metal ion samples, but this trend was comparable to that of the Control. After seven days, the average fluorescence intensities of both the Zn^{2+} sample

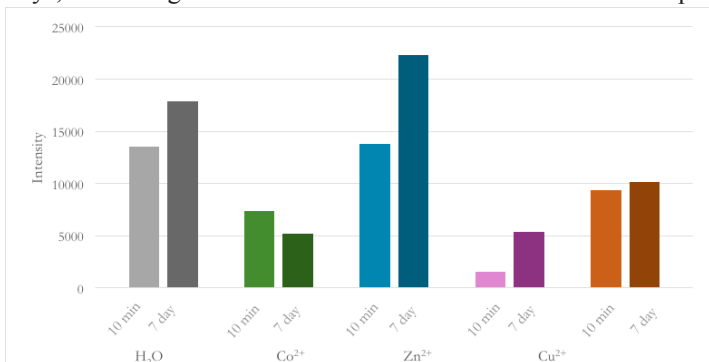


Figure 6. Average fluorescence intensities displayed after ten minutes and seven days of incubation, respectively.

and the Control were both higher than 12000, while the Co^{2+} , Cu^{2+} , and Ni^{2+} samples all displayed average fluorescence intensities that were measured at about 10200 or lower (Figure 6). Therefore, it is safe to note that if an unknown sample of water was scanned using these carbon quantum dots and the fluorescence intensities were 12000 or higher, the sample could either be clean water or water containing metal ions of Zinc.

Due to these massive differences in intensities, continuation with studies furthering dilutions of metal ions to mimic contaminated water with metal ions. Since natural water sources may also have other components potentially affecting the effectiveness of these CQDs, further studies can be done. Additionally, the behaviors seen in ten minutes and seven days also lend to the idea that these nanoparticles could be used for rapid tests, meaning that the carbon quantum dots are not only significant but are capable of working fast to produce detection results of Cobalt, Copper, and Nickel metal ions in water samples. The limit of detection can be found with further trials with diluted metal ion concentrations to compare with specific cut offs for water potability standards in West Africa. Taken together, this work demonstrates that carbon quantum dots synthesized from *S. dulcificum* may be a rapid, accessible, and reliable test for the detection of dissolved metal ions found in water sources of the West African region.

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