# In Situ Synthesis of Bare Silver Nanoparticles on Paper for Copper (II) Ion Detection

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## ABSTRACT

This study synthesized bare silver nanoparticles on paper and evaluated its response to copper (Cu (II)) ions to assess its potential as a colorimetric sensing platform. The nanoparticles were synthesized in situ on paper using silver nitrate and sodium borohydride as a precursor and reducing agent, respectively. No stabilizer or functionalizing agent was added. A two-factor threelevel full factorial design with varying concentrations of reagents was employed in the synthesis process. The resulting sensor was successfully characterized using diffuse reflectance spectroscopy and scanning electron microscopy with elemental dispersive x-ray spectroscopy. The sensor was exposed to varying Cu (II) concentrations ranging from 1 to 30 mM and the developed color changes were analyzed using computer imaging software. The color changes were quantified using mean gray values from the imaging software. Based on the results, as the concentration of Cu (II) ions increased, the final mean gray value of the paper increased as well. The papers were observed to marginally lighten in color potentially due to the decrease in silver atoms or its interaction with copper. The relationship between Cu (II) concentration and the ratio of final and initial mean gray value was determined and although a weak linear relation existed from 1 to 30 mM, a positive slope supported the increase in mean gray value within the range tested. A change in the elemental composition of the paper sensor confirms lightening after its exposure to Cu (II) ions. The sensor also displayed a selective response towards the Cu (II) among other metals tested.

Keywords: Copper, in situ, paper-based, sensor, silver nanoparticles

## INTRODUCTION

Copper in trace amounts is important in many human biological functions such as in iron metabolism and being a cofactor of various redox enzymes. However, it is toxic to the body at high concentrations (Bost et al., 2016). Additionally, it is also associated, directly or indirectly, with the pathogenesis of many neurological diseases such as Menkes disease and Wilson disease (Desai & Kaler, 2008).

Detection and measurement of the concentration of copper in different matrices such as in aqueous solution can be performed using powerful analytical methods. Helaluddin et al. (2016) reviewed the different techniques used for elemental analysis such as atomic

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absorption spectrometry, x-ray fluorescence, and mass spectrometry. These techniques can be employed with good sensitivity and accuracy at the trace level, but they also require high capital costs with instruments involving complex procedures that can only be performed by trained analysts inside established laboratories. Hence, there is a growing body of research dedicated to developing alternative methods for copper detection that are simple, inexpensive, and easy to use.

The development of sensors using nanoparticles has gained wide attention in recent years. Many studies have used silver nanoparticles (AgNP) as colorimetric sensors due to their optical property called localized surface plasmon resonance (LSPR). This refers to the collective oscillation of conducting electrons of the nanoparticles due to electromagnetic radiation. Metallic nanoparticles such as gold and silver nanoparticles exhibit LSPR, thus, they have been used in many research for detecting proteins, organic molecules, and inorganic ions (Vilela et al., 2012).

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There are recent studies that focused on the use of AgNPs for copper detection as Cu(II) ions. Most of the research falls under two main categories: solution-based and paper-based colorimetric assays. The solution-based assay detects Cu(II) ions by its interaction with AgNPs in an aqueous solution. Pourreza and Golmohammadi (2014) reported the use of AgNPs in cloud point extraction for the determination of the metal ions. The emerging use of the different stabilizers was also evaluated in the determination of Cu(II) ions such as citrate-stabilized AgNP (Almaquer & Perez, 2019), dopamine-AgNPs (Ma et al., 2011), and the green synthesis of AgNPs using leaf extract (Kirubaharan et al., 2012). Apart from these solution-based studies, paper-based colorimetric sensors have also been developed where paper is used as a substrate for the sensors. Paper is utilized due to its flexibility, absorbency, biocompatibility and biodegradability, ease of production and modification, low cost, and availability (Nery & Kubota, 2013). Fabrication methods of these paper sensors and its colorimetric response with copper were investigated in different studies. The first case used a modified AgNP embedded in a paper-based analytical device to detect Cu(II) in tap and pond water samples (Ratnarathorn et al., 2012). The complex wax screen-printing method to a simple dipping technique of fabricating decorated AgNPs in the paper sensor also brought about the detection of Cu(II) in samples such as in water, food, and blood (Chaiyo et



1. Paper was cut into small pieces.



6. Dried



2. The paper was soaked in AgNO<sub>3</sub> for 30 minutes.



5. Soaked in water for 1 hour.

al., 2015; Budlayan et al., 2021). The fabrication of simple and low-cost paper sensors for the detection of copper ions makes it more attractive for point-of-use detection of real-world samples.

This study reports the use of bare AgNP synthesized in situ on paper as a potential platform for detecting Cu(II) ions. The in situ synthesis of the bare AgNP on paper was performed using a factorial design for determining the best combination of reagent concentrations to be used. No functionalizing or stabilizing agent was added in the synthesis method. The resulting paper-based sensor was characterized using diffuse reflectance spectroscopy and scanning electron microscopy coupled with energy dispersive x-ray spectroscopy. Response of the bare AgNP paper-based sensor to Cu(II) was determined through color changes in the paper quantified using its mean gray value determined by image analysis. A selectivity test was conducted to compare the response of the sensor to Cu(II) against other common ions.

## **METHODOLOGY**

#### Materials

The following chemicals were used in the study: silver nitrate (AgNO<sub>3</sub>), sodium borohydride (NaBH<sub>4</sub>), copper sulphate (CuSO<sub>4</sub>), activated magnesium oxide (MgO), calcium hydroxide (Ca(OH)<sub>2</sub>), potassium chloride (KCl), barium chloride (BaCl<sub>2</sub>), and ethanol



3. It was then rinsed with ethanol.



4. Immersed in NaBH, for 15 minutes.

Figure 1. Actual photos showing the steps made for the synthesis of the paper sensor.

(C<sub>2</sub>H<sub>5</sub>OH). The reagents mentioned were analytical grade and of high purity. Whatman filter paper no. 41 that was used as the paper substrate has a particle retention of 20-25  $\mu$ m. All aqueous solutions were prepared using distilled water.

### Equipment

Digital imaging analysis was performed using ImageJ software. Characterization of the paper sensor was done by Diffuse Reflectance Spectroscope (Cary 5000) and Scanning Electron Microscope (SEM Hitachi SU3500) coupled with Energy Dispersive X-ray Spectroscope (EDS Bruker XFlash 6 | 30).

## Fabrication of the Bare-AgNP Paper Sensor

The method for fabricating the bare-AgNP paper sensor was adapted from Dankovich and Gray (2011) and He et al. (2003) with minor modifications. Figure 1 shows the actual photos of the steps made in the synthesis of the paper sensor. Briefly, the Whatman no. 41 filter paper was cut into pieces with dimensions of 1  $cm \times 4$  cm. The paper strips were then soaked for 30 minutes in a beaker with 20 mL of AgNO<sub>3</sub> solution. They were then rinsed with pure ethanol to remove excess AgNO<sub>3</sub> that was not absorbed into the filter paper. Afterward, the papers were immersed in a 20 mL cold solution of NaBH4 for 15 minutes and then soaked in distilled water for an hour. It was observed that the white filter paper turned yellow-brown immediately after being immersed in NaBH<sub>4</sub> solution. The paper sensors were then dried and cut into uniform circles with diameters of 6 mm using a puncher.

#### **Experimental Design**

A two-factor three-level  $(3^2)$  full factorial experimental design was employed to optimize the concentration of the bare AgNP attached to the paper substrate. The parameters varied were the concentrations of the AgNO<sub>3</sub> and NaBH<sub>4</sub> which were the precursor metal source and the reducing agent, respectively. The two reagents were identified as the major factors that will influence the silver nanoparticles

Table 1. The  $3^2$  full factorial design employed in the synthesis process.

Factor	Symbol	Values of coded levels		
	-	-1	0	+1
AgNO <sub>3</sub> concentration (mM)	А	1	3	5
NaBH <sub>4</sub> concentration (mM)	В	2	6	10

synthesized in the paper. Determining the appropriate concentrations of AgNO<sub>3</sub> and NaBH<sub>4</sub> was essential in producing an effective paper sensor. The resulting paper sensors were analyzed using ImageJ, an imaging software tool. Table 1 shows the experimental design employed in the synthesis process including their coded levels.

## Image Analysis

Image analysis of all samples in the study followed the same procedure. Treated samples were allowed to develop color changes for 10 minutes before image capture for stability. The samples were placed inside a fabricated monitoring box as seen in Figure 2. This is to obtain a uniform and controlled lighting environment for all samples. Photos were taken using a smartphone (Samsung Galaxy J7 Pro) and analyzed using ImageJ software. The presence of AgNP on paper substrate can be checked in the preliminary trials by the yellow-brown color change of the originally white filter paper. The color change is an indication of the formation of AgNP on the paper (Dankovich, 2014). Comparison of the color intensity among different treatments can be done in ImageJ by converting the original images to 32-bit grayscale images and calculating their mean gray value (MGV). Hence, analysis of the image can be performed by calculating and comparing the MGVs of the samples alongside other characterization techniques. The MGV is the reported result of a grayscale image created by taking the minimum value of the three RGB channels for each pixel. This method is used to create a grayscale image that is more sensitive to changes in brightness than the standard RGB image. The comparison of the lightening and darkening of the paper sensor using MGV provides a more accurate representation of the changes in brightness. The same region of interest was analyzed for all samples



Figure 2. Sketch and measurements of the monitoring box for image capture.

## Characterization of the Paper Sensor

Samples of the bare-AgNP paper sensors were sent to the University of the Philippines Visayas Regional Research Center (UPV RRC) for characterization. Diffuse reflectance spectroscopy (DRS) was used to determine the unique surface plasmon peak of the AgNP on paper. SEM analysis was used to determine the morphological difference pre- and post-synthesis of AgNP, as well as following the addition of copper ions. The size of the synthesized AgNP was also identified through the said analysis. Combined with EDS, the different elements present were visually mapped and the semi-quantitative information regarding their weight percentage distribution in the paper was obtained. The data gathered from the three techniques could confirm the presence of AgNP in the sensor.

#### Colorimetric Response to Cu(II) Ions

**Cu(II) Ion Sensing.** Different concentrations of Cu(II) from 1, 10, 20, 25 and 30 mM were prepared and dropped onto the bare-AgNP paper sensors. Images of the sensors underwent digital imaging analyses to determine the MGV before and after Cu(II) addition. This is to describe the effect of varying concentrations of Cu(II) on the color of the paper. Additionally, a plot profile of the MGV per paper was generated.

Selectivity Test. The following ions were used:  $Cu^{2+}$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Ba^{2+}$ , and  $K^+$ . Different metal cation solutions at 10 mM were dropped onto the paper sensor. Photos were captured and subjected to digital imaging analysis to observe their effect on the paper sensor. Furthermore, the responses of the different ions to the paper sensor were compared quantitatively through their change in MGV.

### **RESULTS AND DISCUSSION**

# Synthesis of Bare AgNP on Paper using Factorial Design

Bare AgNPs or AgNPs, without functionalizing or stabilizing agents, were synthesized in situ on paper. During the experiment, the success of the synthesis process was monitored by observing the color change of the filter paper from white to yellow-brown. The color change is due to the unique optical property of AgNP called surface plasmon resonance (SPR) and is an indication of the formation of AgNP on paper (Dankovich, 2014; Swensson et al., 2018). In this study, upon immersion of the AgNO<sub>3</sub>-wetted paper into the NaBH<sub>4</sub> solution, a color change in the paper from white to yellow-brown was immediately observed. The



Plain filter paper Treated filter paper

Figure 3. Color change of white Whatman 41 filter paper to brown after the AgNP synthesis process. Treated paper image taken from paper treated with 5 mM AgNO<sub>3</sub> and 6 mM NaBH<sub>4</sub>.

comparison of colors before and after the synthesis process is shown in Figure 3.

In terms of AgNP formation, the AgNO<sub>3</sub> served as the silver source, and upon immersion of the AgNO<sub>3</sub>wetted paper to the reducing agent NaBH<sub>4</sub> solution, ionic silver is reduced to silver zero following the chemical equation presented by Mulfinger et al. (2007):

## $AgNO_3+NaBH_4 \rightarrow Ag+\frac{1}{2}H_2+\frac{1}{2}B_2H_6+NaNO_3$ (1)

The aggregation of Ag results in the formation of AgNP. These monodispersed AgNP appear yellow in solution due to their SPR. Moreover, they also exhibit the same yellow-brown color on paper as reported by other similar studies mentioned earlier (Dankovich, 2014; Swensson et al., 2018). It can be noted that the AgNO<sub>3</sub>, NaBH<sub>4</sub>, and ethanol solutions used as reagents in the synthesis process are colorless solutions.

Different factors affect the morphologies and structure in the synthesis of AgNPs in solutions, such as the concentration of reducing agent, the effect of the surfactants and polymers, temperature, AgNO<sub>3</sub> concentration, and the molar ratio of silver precursor and stabilizing agent (Li et al., 2009; AL-Thabaiti et al., 2008; Khodashenas & Ghorbani, 2014). In this study, the AgNPs were synthesized in situ on paper. The concentrations of the precursor and reducing agents as the independent variables were investigated. The synthesis process was subsequently performed using a two-factor three-level (3<sup>2</sup>) full factorial experimental design varying the concentration of AgNO<sub>3</sub> (precursor agent) and NaBH<sub>4</sub> (reducing agent). This was done to determine the best synthesis treatment moving forward with the experiment and to determine both the significance of the factors and their interaction. The response parameter is the MGV of the paper sensor which measures the color intensity of the paper. The



Figure 4. Sample shades of yellow brown converted to 32-bit grayscale image with equivalent MGV.

MGV correlates to the AgNP content of the samples. Several studies have already shown that the formation of AgNP on paper results in the yellow-brown appearance of the paper. A particular study by Chen et al. (2019) showed the connection between increasing AgNP content and the color of the paper samples. The pure paper was white and the increasing AgNP content resulted in the darkening of the brown shade in the paper. Hence, in the synthesis process, a darker shade of yellow-brown is preferred which is indicative of higher AgNP content.

There were nine (9) treatments in the experimental design. To quantitatively compare shades of yellowbrown color produced by each treatment, the photos were analyzed using ImageJ. The photos were first converted to 32-bit grayscale images so that all colors in the images are uniformly converted to shades of gray with varying intensities depending on the original image. Then, the intensities of the gray color in the image were quantified and reflected as a gray value. The mean gray value or MGV refers to the average gray value within a particular selection and is reflective of the brightness or darkness of the selection. For this study, a uniform region of interest was applied to all images.

Shown in Figure 4 is a sample color guide scale that shows the conversion of sample shades of yellow-



Figure 5. Contour plot visualizing the effect of the concentrations of AgNO<sub>3</sub> and NaBH<sub>4</sub> on the mean gray value of the paper sensor.

brown color to grayscale and their equivalent MGV in ImageJ. In the MGV scale used in this study, a plain white color resulted in an MGV of 255 while a plain black color resulted in an MGV of 0. All other resultant images registered MGV between 0 and 255.

With this, the MGVs of the resulting paper for each treatment were determined and were used as the basis for selecting the best treatment. The treatment that resulted in the paper sensor having the lowest MGV was selected and used for succeeding experiments as this corresponded to the paper having the highest AgNP content. Table 2 shows the experimental design and the measured response of the design.

Using two-way ANOVA, results indicate that the means of observations grouped by AgNO<sub>3</sub> concentration are not the same and it is a statistically significant factor with a p-value of  $2.21 \times 10^{-6}$  which is less than alpha of 0.05. The means of observations grouped by NaBH<sub>4</sub> concentration are the same and it is not a statistically significant factor with a p-value of 0.61 which is greater than the alpha of 0.05. The interaction of the two factors is statistically significant with a p-value of  $7.72 \times 10^{-4}$ 

Treatment	Coded matrix		Experimental values		С	Std. dev.
	Α	В	А	В		
1	-1	-1	1	2	108.72	5.20
2	-1	0	1	6	97.93	3.61
3	-1	+1	1	10	95.98	2.30
4	0	-1	3	2	86.89	6.72
5	0	0	3	6	103.95	5.46
6	0	+1	3	10	98.43	5.87
7	+1	-1	5	2	86.22	1.85
8	+1	0	5	6	82.63	3.70
9	+1	+1	5	10	83.19	6.27

Table 2. Experimental design with corresponding MGV per treatment. The standard deviation per treatment was measured from three trials with three replicates each

Table 5. Comparison of absorbance peaks of materials with Agivi obtained through DKS.					
Material	Absorbance	Reference			
	peak				
AgNP colloid	417.4 nm	An et al., 2015			
poly(methyl methacrylate/styrene)/Ag	4238 nm	An et al., 2015			
polysulfone membrane with 2.0 wt% AgNP	418 nm	Andrade et al., 2015			
polysterene/Ag nanocomposite	411 nm	Wang et al., 2008			
Whatman 41 filter paper with AgNP	417 nm	This study			

Table 3. Comparison of absorbance peaks of materials with AgNP obtained through DRS

which is less than the alpha of 0.05. A visual representation of the relationship between the independent variables (concentration of AgNO<sub>3</sub> and NaBH<sub>4</sub>) and the dependent variable (MGV) is shown through the contour map in Figure 5. In agreement with the previous statements, Figure 5 shows that as the concentration of AgNO<sub>3</sub> increases, a significant effect in the MGV is observed as the color lightens. Moreover, the concentration of the NaBH<sub>4</sub> in the y-axis does not greatly affect the dependent variable.

In terms of selecting the best treatment, the paper having the lowest MGV was chosen as this correlates to having the highest AgNP content. As observed in Table 2, treatments 8 and 9 have the lowest average MGV. However, additional statistical tests must be performed because of the proximity of their values. Upon conducting a t-test, the results show that the means of the observations between the two treatments are not statistically different from each other with a p-value of 0.90 which is greater than the alpha of 0.05. With this, treatment 8 (5 mM AgNO<sub>3</sub> and 6 mM NaBH<sub>4</sub>) was chosen because it still registered the lowest MGV and it used less amount of NaBH<sub>4</sub> reagent. This is also consistent with the earlier result that NaBH<sub>4</sub> is not a statistically significant factor, hence choosing a higher 10 mM NaBH<sub>4</sub> solution would only consume more reagent but will not significantly affect the MGV.

#### Characterization of the Bare AgNP Paper Sensor



Figure 6. DRS analysis of the bare AgNP paper sensor showing absorbance peak at 417 nm.

### Diffuse Reflectance Spectroscopy Analysis

The spectral properties of AgNP can be investigated using DRS. The absorbance spectrum of the bare AgNP paper sensor is presented in Figure 6. A scan from 200 to 1600 nm shows a sharp and prominent peak at 417 nm with an absorbance value of 0.87.

The DRS result confirms the presence of bare AgNPs on the paper as the wavelength of the peak position corresponds to AgNPs which is due to their SPR property. Additionally, the sharp and symmetrical peak suggests that the bare AgNP's size distribution is narrow (An et al., 2015). The absorbance peak at 417 nm obtained in this study is very close to the DRS peaks of AgNPs in the literature as presented in Table 3.

### Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy analysis

Presented in Figure 7 is the SEM image of the filter paper (A) and the paper sensor (B). The successful incorporation of the AgNPs on the paper visually turned its color from white to yellow-brown. This is supported by the attachment of the bare AgNP in the cellulosic fibers of the paper (B) after the synthesis process. The well-distributed AgNPs prove that the fibers of the paper provide a good binding site for metallic nanoparticles. Notably, Figure 8 shows a magnified image of the paper sensor with AgNP particles with an approximate particle size range of 96 nm to 127 nm.

Furthermore, the EDS spectrum also confirms the presence of AgNP in the paper sensor. Figure 9 reports a strong signal of the silver peak at 3 keV, which is typically detected for metallic silver nanoparticles (Liang et al., 2017), and it accounts for 2.05 wt%. The elemental mapping in Figure 10 shows that the relative distribution of the silver, represented as green dots, are spread evenly within the paper. This further suggests that the chosen paper platform, Whatman no. 41, is able to keep the nanoparticles within its cellulose fibers. The presence of AgNP affirms the result of the DRS analysis shown in Figure 6.



Figure 7. SEM images of (A) the plain filter paper showing its porous structure and clean fibers and (B) the paper sensor showing the synthesized AgNP deposited on the fibers appearing as white spots.



Figure 8. A magnified SEM image of the paper sensor showing an approximate AgNP particle size range of 96 nm to 127 nm.



Figure 9. EDS spectrum and weight percentage distribution of the elements in the bare AgNP paper sensor.



Figure 10. EDS elemental mapping of the (A) area of interest of the sensor, showing the (B) distribution of Ag.

## Response to Cu(II) Ions

**Change in Mean Gray Value.** To test the potential of the platform for Cu(II) sensing application, the papers were exposed to varying Cu(II) concentrations. Figure 11 shows the effect of increasing Cu(II) concentration to the MGV of the paper sensor.



Figure 11. Effect of increasing Cu (II) concentration on the final MGV of the bare AgNP paper-based sensor. Top row photos are the actual images taken inside the monitoring box while bottom row photos are the corresponding grayscale images. Bar graph represents the MGV profile within each paper sample.

To generate Figure 11, photos of the actual paper sensors were converted to grayscale images. Then in ImageJ analysis, the grayscale images were set against a black background to remove gray values that do not belong to the region of the paper sensor. Then, a linear region of interest was drawn to obtain a plot profile of the MGV across the papers. In the figure, as the concentration of Cu(II) ions is increased from 1 to 30 mM, the final MGV of the bare AgNP paper appears to be increasing as well. The increase in MGV indicates the lightening of the brown color of the papers within the range specified.

In terms of visual monitoring, comparing the paper exposed to 1 mM and the paper exposed to 30 mM Cu(II), one can observe that the brown shade of the 30 mM Cu-exposed paper is lighter compared to that of the 1 mM Cu-exposed paper. However, the color changes are difficult to detect by the naked eye for other tested concentrations between 1 and 30 mM. Hence, the assistance of software for image analysis is very important. Using ImageJ, the MGV of the paper exposed to 30 mM Cu(II) registered a higher MGV compared to paper exposed to 1 mM Cu(II). This increase in MGV is consistent with the observed lightening of the brown shade of the paper. The relationship between MGV and the shades of color was presented earlier in Figure 4.

## Relationship of Cu(II) Concentration and Mean Gray Value (MGV)

A plot of the ratio of the mean gray values  $(MGV_{final}/MGV_{initial})$  and Cu(II) concentration was generated and is presented in Figure 12. Each point in the graph represents the average of three trials with each trial having three replicates. The error bars represent the standard deviation.



Figure 12. Relationship of  $MGV_{final}/MGV_{initial}$  and Cu (II) concentration up to 30 mM. Generating a linear profile results to a coefficient of determination value of 0.7071 and a positive slope of 0.0023.

The plot in Figure 12 shows that as the Cu(II) concentration is increased, the ratio  $MGV_{final}/MGV_{initial}$  appears to be increasing as well. If a linear profile is generated for the two parameters, the coefficient of determination is 0.7071 with a positive slope of 0.0023. The positive slope affirms that as the Cu(II) concentration is increased, the MGV ratios of the paper increase as well. This translates to the papers generally lightening in color when exposed to Cu(II) within the tested range. However, the value of the coefficient of determination implies that the increase in the MGV ratios is not strongly linear to Cu(II) concentration of the tested range.

#### **Elemental Composition Changes**

The response of the bare AgNP paper-based sensor after its exposure to Cu(II) solution was evaluated using SEM-EDS analysis. SEM analysis shows that the filter paper retains its porous structure after addition of 100 mM Cu(II) solution. On the other hand, EDS analysis shows that unlike the EDS spectrum of the paper sensor seen in the previous section, Figure 13 presents the detection of the Cu in its EDS spectrum as expected due to its exposure. The elemental mapping of the copperexposed paper sensor presented in Figure 14 shows the



Figure 13. EDS spectrum of the paper sensor after exposure to 100 mM Cu (II) solution



Figure 14. EDS elemental mapping of the (A) area of interest of the sensor exposed to 100 mM Cu(II) solution showing the presence of (B) silver in green dots and (C) copper in blue dots.

distribution of the elements of the area of interest - green dots for silver and blue dots for copper. The weight percentage distribution reported a 5.18 wt% for copper. Moreover, the introduction of Cu(II) caused a decrease in the percent distribution of the silver. Compared to the previous 2.05 wt % reported, only 0.69 wt% silver was detected after its addition. The decrease in silver percentages could explain why the papers were slightly lighter in color after Cu(II) exposure. Potentially, complexes were formed between the silver and copper ions that caused the alteration of the morphologies and characteristics of the nanoparticles, thus, resulting in the decrease of its wt % distribution in the sensor.

#### **Response Comparison with Other Common Ions**

The response of the bare AgNP paper to other common ions was investigated and plotted in comparison to Cu (II) ions. The plot comparison is shown in Figure 15. The bars represent the average of three trials while the error bar represents the standard deviation.

Based on Figure 15, only Cu(II) showed a positive change in MGV among the tested ions. This indicates that exposure to Cu(II) generally lightens the yellow-



Figure 15. Comparison of responses among different common ions show only Cu (II) registered a positive increase in MGV.

brown color of the paper while the effect of the other ions is the reverse. This implies that the bare AgNP paper-based sensor behaves differently when exposed to a low concentration of Cu(II) ions than the rest of the tested ions.

## CONCLUSION

Bare AgNP paper sensor was successfully fabricated and characterized in terms of its spectral and morphological properties, as well as its elemental properties. Silver nanoparticles were synthesized in situ the paper using the best concentrations of the precursor and reducing agent as identified through a full factorial design. Different techniques such as DRS, SEM, and EDS were utilized that confirm the presence of AgNP on the fibers of the filter paper. SEM-EDS analysis also shows that the filter paper retains its porous structure before and after exposure to copper ions. In addition, MGV analysis using ImageJ processing software, and SEM-EDS analysis were performed to test the response of the filter paper to the copper ions. Lightening of the paper sensor was observed after exposure to copper ions compared with other tested ions, however, as a recommendation, testing incorporating and functionalizing agents could improve the overall response of the sensor.

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## **AUTHORS' CONTRIBUTIONS**

FEA conceptualized and secured funding for the study through the Small Budget In-house Research Grant. All authors contributed to the data gathering, manuscript writing, and analysis. Also, all authors checked and approved the final manuscript.

## **CONFLICT OF INTEREST**

The authors declare no conflict of interest.

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