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Sugar-Reduced Gelatin-Capped Silver Nanoparticles with High Selectivity for Colorimetric Sensing of Hg^{2+} and Fe^{2+} Ions in the Midst of Other Metal Ions in Aqueous Solutions.

Bambesiwe M. M. May[1] *and Oluwatobi S. Oluwafemi*[1,2]

[1] Centre for Nanomaterials Science Research, University of Johannesburg, Johannesburg, South Africa.
[2] Department of Applied Chemistry, University of Johannesburg, P.O. Box 17011, Doornfontein 2028, Johannesburg, South Africa.
*E-mail: oluwafemi.oluwatobi@gmail.com

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Green synthesized dextrose and maltose-reduced silver nanoparticles (Ag-NPs) were investigated for colorimetric sensing of metal ions at different concentrations and reaction time. The synthesized Ag-NPs were characterized using UV-Visible spectroscopy (UV-Vis), Fourier transform Infra-red spectroscopy (FTIR), transmission electron microscopy (TEM) and dynamic light scattering (DLS). Both maltose and dextrose-reduced Ag-NPs were highly sensitive and selective to Hg^{2+} and Fe^{2+} ions over other metal ions at higher metal ion concentration. This was accompanied with a colour change from yellowish solution to colourless for Hg^{2+} ions and from yellowish solution to greenish for Fe^{2+} ions. Our findings also showed that dextrose-reduced Ag-NPs resulted in better colorimetric sensing of metal ions than maltose-reduced Ag-NPs. Both Ag-NPs solutions were highly sensitive and selective towards Hg^{2+} ions at lower concentration up to 10^{-12} M with a linear regression coefficient value (R^2) of 0.9792 and 0.9740 for maltose and dextrose reduced Ag-NPs respectively. The study on variation of reaction time showed that the sensing reaction can be carried out within a short reaction time of 30 s.

Keywords: Green synthesis; silver nanoparticles; maltose; dextrose; metal ion; colorimetric sensor

1. INTRODUCTION

Over the past decades researchers have shown a lot of interest in noble metal nanoparticles (NPs) due to their unique properties and applications in medicine, biology, catalysis and electronic applications. Many methods have been reported for the synthesis of metal nanoparticles but the most reported method is the chemical reduction method. This usually involves the reduction of metal ion

using different reducing agents such as borohydrides, hydroxylamine hydrochloride, trisodium citrates and dimethylformamide [1,2] and capping agents such as polyvinyl pyrrolidine (PVP) polyethylene glycol and poly(methyl methacrylate) [3-5] to stabilize the as-synthesized metal nanoparticles. Though, high quality metal NPs have been prepared by this method however, some of the reducing and stabilizing agents used have raised some serious environmental concerns. Hence, there is need to implement green chemistry principle in the synthesis of metal NPs in order to reduce environmental toxicity and, maximize safety and efficiency.

Raveendran *et al*, reported the first completely green synthesis of Ag-NPs following green chemistry principles. In their reaction, glucose and starch were used as reducing and stabilizing agents respectively for the synthesis of stable Ag-NPs [6]. Darroudi et al., also reported green synthesis of Ag-NPs without the use of an accelerator by reducing Ag^+ ions in aqueous gelatin media with and without glucose as a reducing agent [7]. Gelatin was used as a stabiliser due to its excellent stabilizing functional groups and, good biocompatibility and biodegradability. Another green synthetic measure is the biosynthesis of metal nanoparticles. Biological synthesis of silver nanoparticles by the reduction of silver ions using kiwifruit juice as the reducing and stabilizing reagent at room temperature was reported by Gao *et al*., [8]. In another development, our group reported size tunable green synthesis of maltose-reduced Ag-NPs without the use of an accelerator or complexing agent. By varying the reaction time and the concentration of the silver precursor, smaller Ag-NPs with an average particle diameter of about 3.76 nm were obtained at 24 hours reaction time at higher Ag precursor concentration [9].

Heavy metals enter the environment due to increasing industrial activities and have been found to be potential pollutants even at trace concentrations. They are non-biodegradable and can accumulate in the food chain, which serves as a treat to the environment and human health [10]. Therefore, it is important that these ions are detected and measured in both environmental and biological samples under aqueous conditions with high sensitivity and selectivity without interference of other metal ions. Several effective methods with excellent sensitivity and multi-element analysis have been reported for the detection of heavy metal ions using various analytical instruments [11-13]. However, the cost effectiveness and time consuming procedure in addition to the fact that, these methods involves non portable accessories and are skill dependent poses a significant challenge. Hence, there is need for an alternative, cost effective protocol with high sensitivity and non-skill dependent approach.

Metal nanoparticles can be considered an optical probe where nanoparticles at nanomolar concentration allow sensitive detection with minimal consumption of materials. Recently metal nanoparticles especially silver nanoparticles (Ag-NPs) and gold nanoparticles (Au-NPs) have been used extensively for colorimetric detection of heavy metal ions. These types of colorimetric sensor offer rapid tracking of valuable and toxic metal ions in environmental samples/systems in addition to their cost effectiveness and high sensitivity [12-15]. Most of the reported method involve the use of Ag-NPs probe generated via sunlight irradiation and protected by amino acid such as tryptophan, glutathione and L-tyrosine for the detection of Hg, Pb and Mn ions [16-20]. Hence, in the present work, the use of completely green synthesized maltose and dextrose-reduced Ag-NPs without any accelerator for fast colorimetric sensing of metal ions is investigated. The as-prepared Ag-NPs are characterized using various techniques. The use of gelatin as capping agent offers good water

dispersibility, biocompatibility, and stability. In addition, the as-synthesised Ag-NPs are highly selective towards Hg^{2+} and Fe^{2+} ions over other metal ions at higher metal ion concentration.

2. MATERIALS AND METHODS

2.1. Chemicals

$AgNO_3$, gelatin and maltose as well as LiCl, KCl, $CaCl_2$, $BaCl_2$, $CoCl_2$, $HgCl_2$, $MnCl_2$, $Pb(NO_3)_2$, $FeSO_4$, $MgCl_2$, and $Cr_2(SO_4)_2$ salts were obtained from Sigma Aldrich and used as received without further purification.

2.2. Synthesis of sugar-reduced Ag-NPs

The synthesis was based on our previous report [9], with slight modification. In a typical reaction, 1 % (w/v) of gelatin solution was prepared in a 100 mL flask. The solution was stirred and heated at 40 $^{\circ}$C to obtain a clear solution. Then, 5 mL of 1 M silver nitrate solution was added to the gelatin solution under continuous stirring to obtain Ag^{+}/gelatin complex solution. 10 mL of 2 M maltose solution was added to the Ag^{+}/gelatin complex solution under continuous stirring. The temperature of the solution was increased to 75 ^{o}C and aliquots were drawn at different reaction times. The same procedure was followed for the synthesis of dextrose-reduced silver nanoparticles, where 2 M of dextrose was used as reducing agent.

2.3. Characterization

UV–Visible spectrophotometer was used to carry-out absorption spectra in the 200–1100 nm wavelength range. The measurement was carried out using quartz cuvettes (1 cm path length) at room temperature. Transmission electron microscope (TEM) measurements were carried out using a TEM operating at 200 KV. The IR spectra for the synthesized Ag-NPs was measured using a Perkin Elmer FT-IR instrument at room temperature. The dynamic light scattering was carried out using Malvern zetasizer Nano series.

2.4. Metal ion sensing study

Solutions of 10^{-1}, 10^{-3}, 10^{-5} M metals ion (Li^{+} , K^{+}, Mg^{2+}, Ca^{2+}, Ba^{2+}, Fe^{2+}, Cr^{3+}, Co^{2+}, Pb^{2+}, Hg^{2+}, and Mn^{2+}) were prepared separately. 1 mL of each metal ion solution was added to 3 mL of diluted Ag-NPs solution and the resulting mixture was left to react for 30 s followed by analysis using UV-Vis spectrophotometer.

3. RESULTS AND DISCUSSION

3.1. Characterisation of sugar-reduced Ag-NPs

During the synthesis, the gelatin solution turned into a clear solution after being heated and stirred at 40 ^{0}C. There was no colour change observed after silver nitrate and maltose/dextrose solution was added. However, as the reaction proceeded, the solution turned light brown after 10 mins and then became dark brown as the reaction continued. The colour change of the solution was due to the reduction reaction of Ag^{+} ions to Ag^{O}, indicating the formation of Ag-NPs of different particle sizes. Figure 1 shows the absorption spectra of maltose and dextrose-reduced Ag-NPs at different reaction time. The synthesized Ag-NPs exhibited an absorption peak characteristic of silver SPR peak from 422 to 433 nm for maltose-reduced Ag-NPs and from 428 nm to 420 nm for dextrose-reduced Ag-NPs as the reaction time increased (Table 1). Broad SPR peaks were observed at the beginning of the reaction, which later become narrow as the reaction time increased.

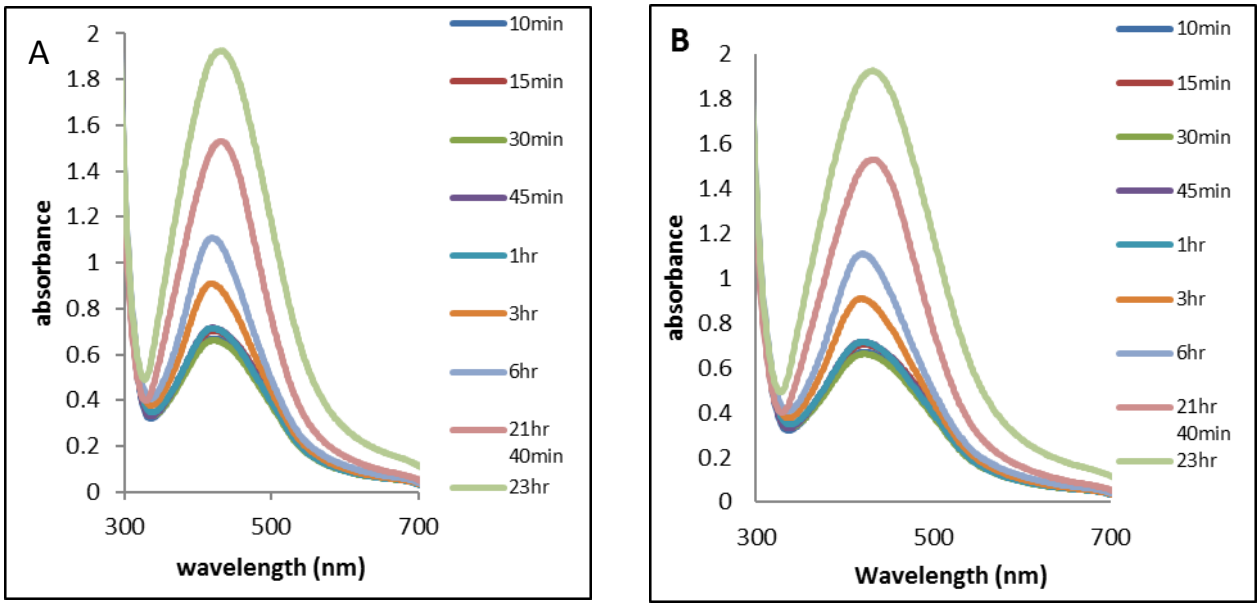


Figure 1. Absorption spectra of maltose (A) and dextrose-reduced (B) Ag-NPs at different reaction time.

This indicates the formation of Ag-NPs with broad size distribution at the initial stage of the reaction and narrow size distribution at the later stage. The increase in the intensity of the SPR peak as the reaction time increase is attributed to continuous reduction of Ag^{+} ions to produce Ag-NPs and thus, increase in the concentration of Ag-NPs present in the solution. During the formation of maltose-reduced Ag-NPs from 10 min to 3 h, a blue shift of the SPR peak from 422 nm to 419 nm was observed indicating a decrease in particle size. As the reaction time increased from 6 h and beyond, the SPR peak become red-shifted shifted from 419 nm to 431 nm indicating increase in particle size. The initial blue shifting is due to high rate of reduction reaction attributed to the high reducing saccharide concentration in the solution. This resulted in the formation of smaller sized Ag-NPs. The larger

particles produced at the later stage is attributed to Ostwald ripening i.e. dissolution of smaller particles due to their high surface energy [9]. The spectra for the dextrose-reduced Ag-NPs, shows a red shift in the SPR peak position from 428 nm to 431 nm as the reaction time increased from 10 min to 6 h indicating increase in particle size. After 6 h, the SPR peak became blue-shifted indicating decrease in particles size. This is attributed to digestive ripening. The SPR peak position remain constant at 23 h and beyond for the two reactions indicating the end of the reduction reaction.

Table 1. Optical properties of maltose (left) and dextrose (right) reduced Ag-NPs as a function of time.

Time (min)	**SPR Peak position (nm)**	**SPR Peak Absorbance**
10min	428	0.8122
15min	431	0.8064
30min	430	0.8079
45min	431	0.9408
1h	430	0.7948
3h	431	1.0243
6h	431	1.3748
21h 40 min	419	2.3131
23h	420	2.6267
Time (min)	**SPR Peak position (nm)**	**SPR Peak Absorbance**
10min	422	0.6699
15min	422	0.7032
30min	422	0.6613
45min	421	0.7156
1h	421	0.7144
3h	419	0.9080
6h	420	1.1078
21h 40 min	433	1.5301
23h	431	1.9269

The possible chemical reaction involved for the formation of sugar-reduced gelatin-capped silver nanoparticles is given in scheme 1. In this reaction, maltose hydrolysis resulted in two molecules of glucose which serves as the reducing agent. The glucose reduces Ag^+ ions to Ag^0, and in the process become oxidized to gluconic acid. The electrochemistry of this reaction is given in scheme 2. The potential for the overall reaction is 0.750 V thus thermodynamically, the reaction is spontaneous (ΔG is –Ve). One way of increasing the reaction rate which can also control the particle size is by adding ammonia (NH_3) to the solution to produce $Ag(NH_3)_2^+$ complex ion [21]. The diamine silver ion complex is a weaker oxidising agent with considerable smaller reduction potential than Ag^+ ion (Scheme 3). Thus, the reducing power of glucose is enhanced in the presence of ammonia. In our

reaction, the use of ammonia was avoided because it is a very corrosive and hazardous chemical. Its potential environmental and biological risks are a source of concern therefore we used maltose. Hydrolysis of maltose increased the concentration of the reducing saccharides in the reaction system (Scheme1). Thus, the number of H^+ ions released into the reaction system per hydrolysis increased (Scheme 4). This resulted in an increase in the rate of the reaction and production of large number of smaller sized Ag NPs. Therefore, the use of ammonia to lower the reduction potential of the Ag+ ions was avoided.

$$Ag^{+}_{(aq)} + \text{gelatin}_{(aq)} \longrightarrow [Ag(\text{gelatin})]^{+}_{(aq)} \quad (1)$$

$$C_{12}H_{22}O_{11(aq)} \xrightarrow{H_2O} 2C_6H_{12}O_{6\,(aq)} \equiv 2C_5H_{11}O_5\text{-}CHO_{(aq)} \quad (2)$$

$$2[Ag\,(\text{gelatin})]^{+}_{(aq)} + 2C_5H_{11}O_5\text{-}CHO_{(aq)} \longrightarrow \text{gelatin capped Ag-NP(s)} + 2C_5H_{11}O_5\text{-}COOH_{(aq)} \quad (3)$$

Scheme 1. Possible chemical reaction involved in the formation of gelatin capped -maltose- reduced silver nanoparticles. Eq. (1) is the formation of gelatin-silver ion complex.

$$2\,Ag^{+} + 2e^{-} \longrightarrow 2Ag \qquad E^{o}_{red} = 0.800\ V \ \ldots\ldots\ldots \quad (4)$$

$$C_6H_{12}O_6 + H_2O \longrightarrow C_6H_{12}O_7 + 2H^{+} + 2e^{-} \qquad E^{o}_{ox} = -0.050\ V \ldots\ldots \quad (5)$$

$$2\,Ag^{+} + C_6H_{12}O_6 + H_2O \longrightarrow 2Ag + C_6H_{12}O_7 + 2H^{+} \qquad E^{o} = 0.750\ V \ldots\ldots \quad (6) = (4)+(5)$$

Scheme 2. The half reactions and the standard reduction potentials for reduction of Ag^+ by glucose under standard-sate condition.

$$2Ag(NH_3)_2^{+} + 2e^{-} \longrightarrow 2Ag + 2\,NH_3 \qquad E^{o}_{red} = 0.373\ V \ldots\ldots\ldots \quad (7)$$

$$C_6H_{12}O_6 + H_2O \longrightarrow C_6H_{12}O_7 + 2\,H^{+} + 2e^{-} \qquad E^{o}_{ox} = 0.600\ V \ldots\ldots\ldots \quad (8)$$

$$2Ag(NH_3)_2^{+} + C_6H_{12}O_6 + H_2O \longrightarrow 2Ag + C_6H_{12}O_7 + 2NH_4 \qquad E^{o} = 0.973\ V \ldots \quad (9)$$

Scheme 3. The half reactions and the standard reduction potentials for reduction of Ag^+ by glucose in the presence of ammonia solution.

$$4Ag^{+} + 4e^{-} \longrightarrow 4Ag \qquad E^{o}_{red} = 0.800\ V \ \ldots\ldots\ldots \quad (10)$$

$$2C_6H_{12}O_6 + 2H_2O \longrightarrow 2C_6H_{12}O_7 + 4H^{+} + 4e^{-} \qquad E^{o}_{ox} = -0.050\ V \ldots\ldots\ldots \quad (11)$$

$$4Ag^{+} + 2C_6H_{12}O_6 + 2H_2O \longrightarrow 4Ag + 2C_6H_{12}O_7 + 4H^{+} \qquad E^{o} = 0.750\ V \ldots\ldots \quad (12)$$

Scheme 4. The half reactions and the standard reduction potentials for reduction of Ag^+ by maltose.

The typical TEM micrograph for both maltose and dextrose-reduced Ag-NPs (Fig. 2) show that the as-synthesised Ag-NPs are small, well dispersed and spherical in shape. The hydrodynamic particle size for maltose-reduced Ag-NPs is between; 8.7 nm to 58.8 nm with an average particle diameter of 11.88 ± 1 nm (Fig.3 A) and between 13.5 nm to 68.1 nm with an average particle diameter of 18.17 ± 1 nm for dextrose-reduced Ag-NPs (Fig.3B). Both the TEM and dynamic light scattering (DLS) result revealed that maltose-reduced Ag-NPs were smaller in size than the dextrose-reduced Ag-NPs. This is

attributed to the reducing saccharide concentration. During the reaction, maltose hydrolysed into two glucose molecules. This increase the amount of reducing saccharide in the reaction medium and thus, increase in the rate of reduction reaction. In the case of dextrose, the hydrolysis produced lower concentration of reducing saccharide in the solution and hence lower rate of reduction.

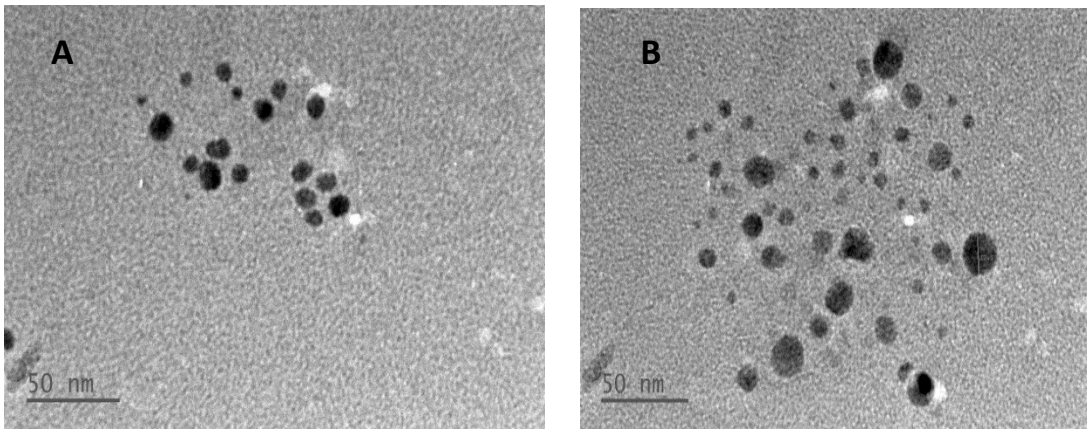
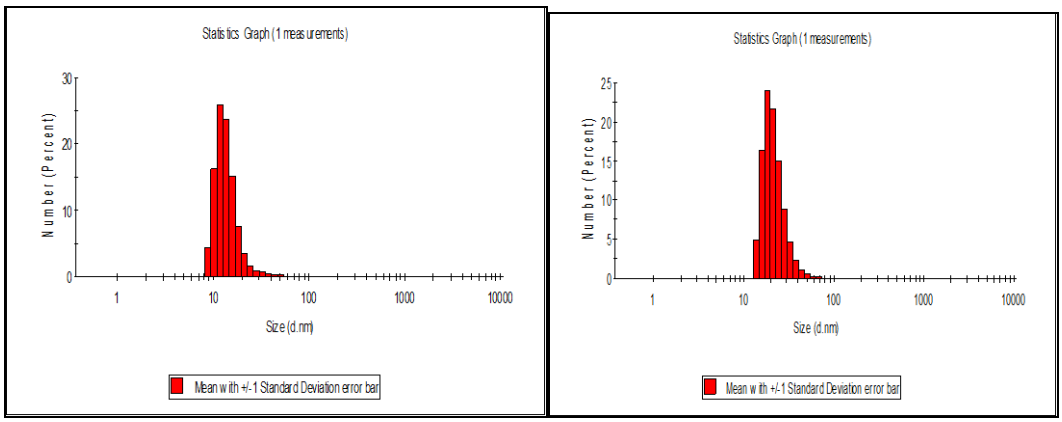


Figure 2. Typical TEM micrographs of maltose (A) and dextrose (B) -reduced Ag-NPs.



A B

Figure 3. Hydrodynamic particle size distribution of maltose (A) and dextrose (B)-reduced Ag-NPs.

The surface chemistry of the synthesized Ag-NPs was investigated using FT-IR spectroscopy to confirm the capping of Ag-NPs with gelatin (Fig. 4). The polyamide protein with characteristic absorption bands for amide I at 1626 cm^{-1}, amide II at 1527 cm^{-1}, amide III at 1234 cm^{-1} and hydrogen bonding at 3281 cm^{-1} were seen in all the spectra. The broad hydrogen bond absorption peak found at 3281 cm^{-1} corresponds to both the O-H stretching vibration of O-H group and N-H stretching due to molecules bonded to N-H in gelatin. The amide I vibration mode is mainly a C=O stretching vibration coupled with contributions from the C-N stretch, C-N deformation, and in-plane N-H bending modes, which was found at 1641cm^{-1}. The peak at 1054 cm^{-1} is attributed to the C-O vibrations from the gelatin. The IR-spectra comparison shows a shift of the O-H group and amide II group from 3182 cm^{-1} to 3333 cm^{-1} and 1527 cm^{-1} to 1455 cm^{-1}, respectively for maltose-reduced Ag-NPs and while a shift

from 3182 cm^{-1} to 3208 cm^{-1} and 1527 cm^{-1} to 1426 cm^{-1}, respectively was obtained for dextrose-reduced Ag-NPs. The shift suggests electrostatic interaction between Ag-NPs and the gelatin thus confirming the capping of the Ag-NPs by gelatin.

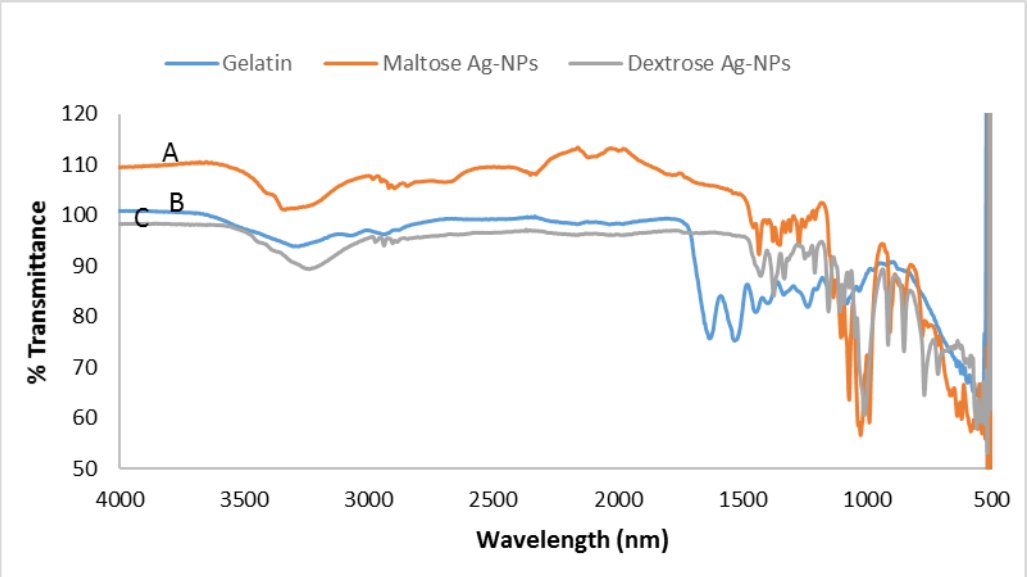


Figure 4. FT-IR spectra of gelatin (A), maltose-reduced Ag-NPs (B) and dextrose-reduced Ag-NPs (C).

3.2. Metal ion sensing ability of Ag-NPs

The sensitivity and selectivity of the maltose and dextrose-reduced Ag-NPs towards various metal ions were studied. A UV-Vis absorption spectra (Fig.5 & 6) were obtained to monitor the change in the absorbance after the addition of the various metal ions after 30 s reaction time. The results showed that the Ag-NPs were sensitive to all the metal ions as seen by the change in the intensity of the SPR peak position after the addition of the metal ions. In addition, the position of the SPR peaks became blue-shifted after the addition of the various metals, indicating decrease in particle size. However, the colorimetric response of both Ag-NPs (Fig. 5 & 6) showed colour changes only for $Hg^{2+}$and Fe^{2+} ions. This indicates the selectivity of the as-prepared Ag-NPs for the two metal ions over other metal ions. Addition of Hg^{2+} ion to both Ag-NPs solutions changed the colour of the solution from yellowish brown to colourless. This change in colour was accompanied with remarkable decrease in the absorbance of the Ag-NPs. This has been attributed to the disappearance of the Ag-NPs in the solution due to the redox reaction between zero valent Ag and Hg^{2+} ions. The Ag-NPs were oxidised to form Ag^{+} and Hg^{2+} reduced to Hg atom. Similar observation had been reported by Annadhasan *et al.*, [20].

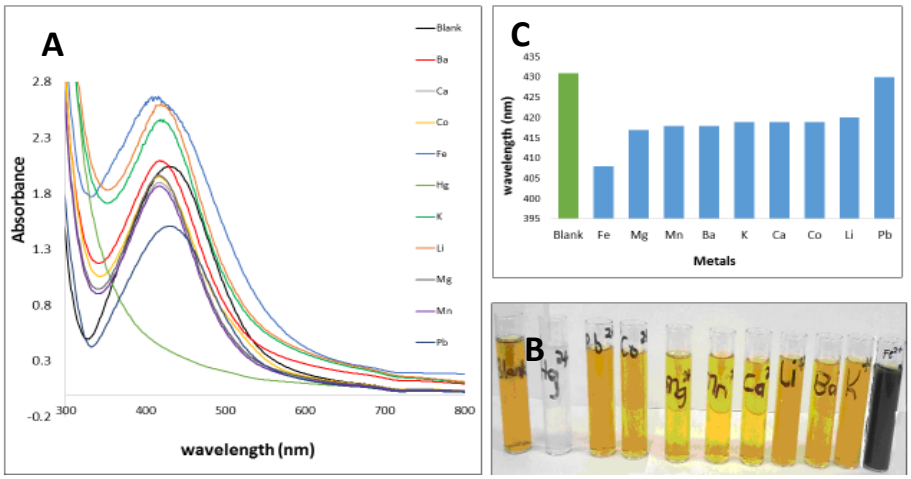


Figure 5. (A) Absorption spectra, (B) colorimetric response after addition of various metal ions to maltose-reduced Ag-NPs (From far left: Blank, Hg^{2+}, Pb^{2+}, Co^{2+}, Mg^{2+}, Mn^{2+}, Ca^{2+}, Li^{+}, Ba^{2+}, K^{+}, and Fe^{2+}) and (C) the change in the SPR peak position.

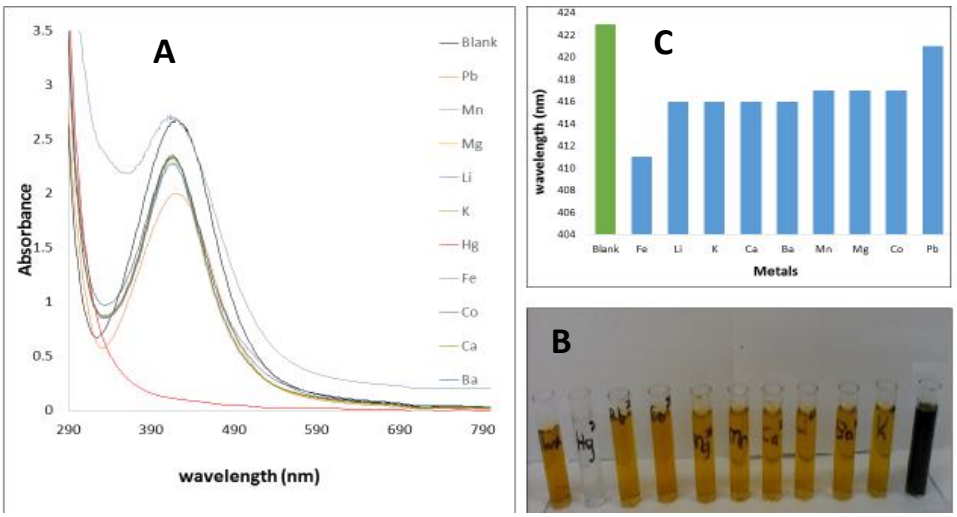
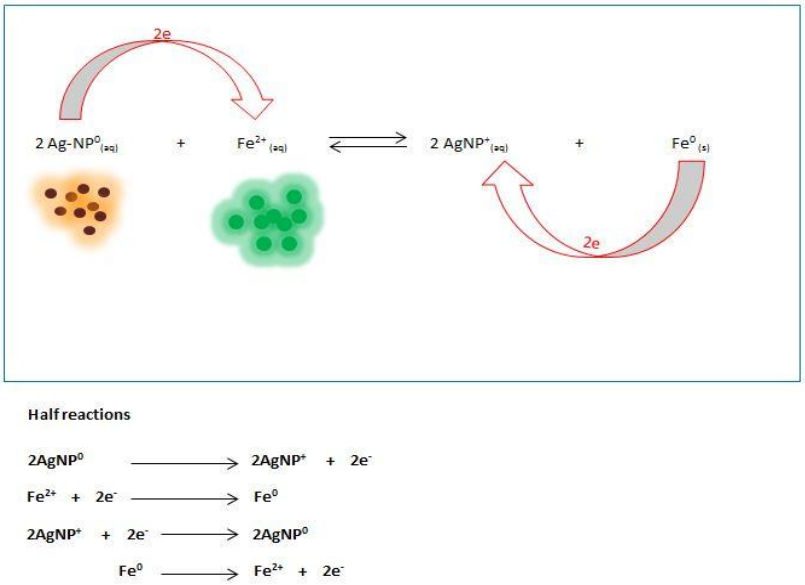


Figure 6. (A) Absorption spectra, (B) colorimetric response after addition of various metal ions to dextrose-reduced Ag-NPs (From far left: Blank, Hg^{2+}, Pb^{2+}, Co^{2+}, Mg^{2+}, Mn^{2+}, Ca^{2+}, Li^{+}, Ba^{2+}, K^{+}, Cr^{3+} and Fe^{2+}) and (C) the change in the SPR peak position.

Addition of Fe (II) ion changed the colour of both Ag-NPs solution from yellowish brown to dark green. This colour change was accompanied by an increase in the SPR peak intensity with a significant decrease in the SPR peak position from 431 to 408 nm for maltose-reduced Ag-NPs (Fig.5 C) and from 423 nm to 411 nm for dextrose-reduced Ag-NPs (Fig. 6C). This decrease in the SPR peak position could be attributed to the formation of smaller Ag-NPs while the enhanced intensity is attributed to the increased concentration of Ag-NPs in the solution. The addition of Fe^{2+} solution resulted in a redox interaction between the Fe^{2+} and Ag-NPs present in the solution. After the addition of Fe^{2+} into the solution, the Ag-NPs reduced the Fe $^{2+}$ to zero valent iron (Fe^{o}) while itself was oxidised to Ag^{+}. The Fe^{o} in the solution being a very strong reducing agent than the Ag^{+} immediately

reduced the as-formed Ag^{+} ion to silver nanoparticles while itself was oxidised to Fe^{2+}. The formation of this Fe^{2+} ions is responsible for the final green solution obtained during the reaction. The further reduction of the original silver nanoparticle after It's oxidation to Ag^{+} by the Fe^{O} led to the formation of smaller particle size. Hence the SPR peak position became blue-shifted. The increase in intensity is attributed to the increase in the number of Ag-NPs present in the solution. The mechanism of this reaction is given in Scheme 5.



Scheme 5. Mechanism for the formation of green colour after addition of Fe^{2+} to the solution of Ag-NPs.

The selectivity and sensitivity of the maltose and dextrose-reduced Ag-NPs was further studied at lower metal ion concentrations of 10^{-3} M. The absorption spectra (Fig 7) revealed that both maltose and dextrose reduced Ag-NPs were sensitive to all the metal ions at this concentration. This is indicated by the decrease in the SPR peak intensity. However, the Ag-NPs solutions were found to be more sensitive and selective to Hg^{2+} ion compared to other metal ions. This is shown by the remarkable decrease in the SPR peak intensity after the addition of Hg^{2+} ions. The physical appearance shows that there was a slight colour change after the addition of Hg^{2+} ions to maltose-reduced Ag-NPs (Fig. 7A inset) while a significant colour change from yellowish brown to light yellow was observed after the addition of Hg^{2+} ions to dextrose-reduced Ag-NPs (Fig. 7B, inset). The decrease in the SPR peak intensity after the addition of Hg^{2+} ion to the Ag-NPs solution was accompanied with hypochromic shift in the SPR peak position. This indicates reduction in the concentration of Ag-NPs present in the solution and the presence of smaller Ag-NPs. The decrease in the particle size is attributed to the oxidation of the Ag-NPs by Hg^{2+} ion to produce Ag^{+} ion thus, decreasing the amount of Ag-NPs in the solution. The higher % degradation of dextrose reduced Ag-NPs and slight colour change observed indicates higher sensitivity of dextrose-reduced Ag-NPs towards Hg^{2+} ions than the maltose-reduced Ag-NPs. This is attributed to the high passivation of smaller sized maltose-reduced Ag-NPs by the capping agent than the larger sized dextrose-reduced

Ag-NPs. Thus, the Hg^{2+} ion can interact easily with dextrose-reduced Ag-NPs since they are less passivated. This make these Ag-NPs prone to easy degradation compared to the maltose-reduced Ag-NPs

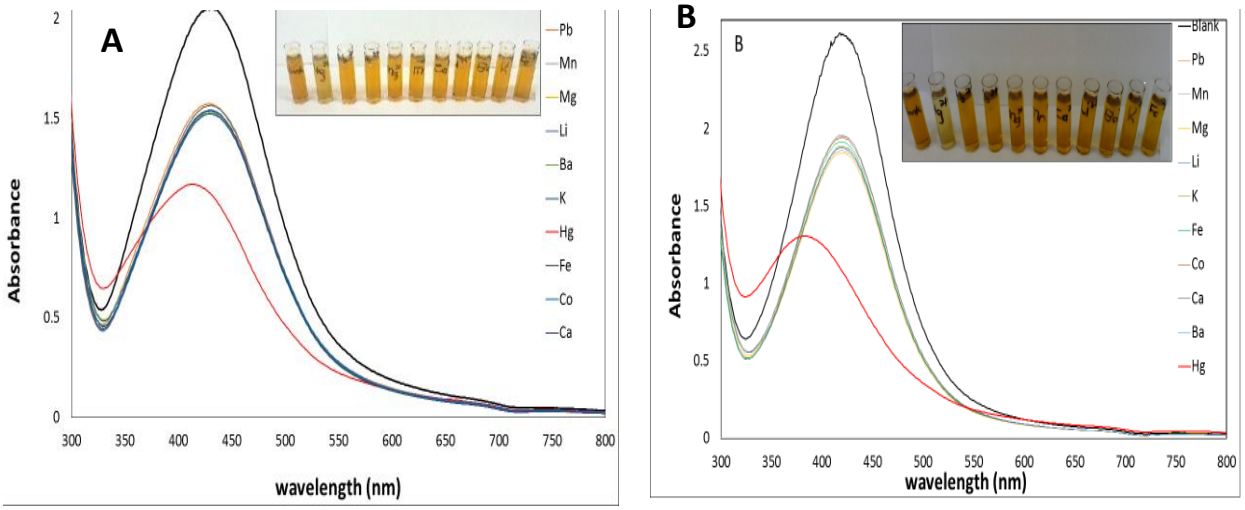
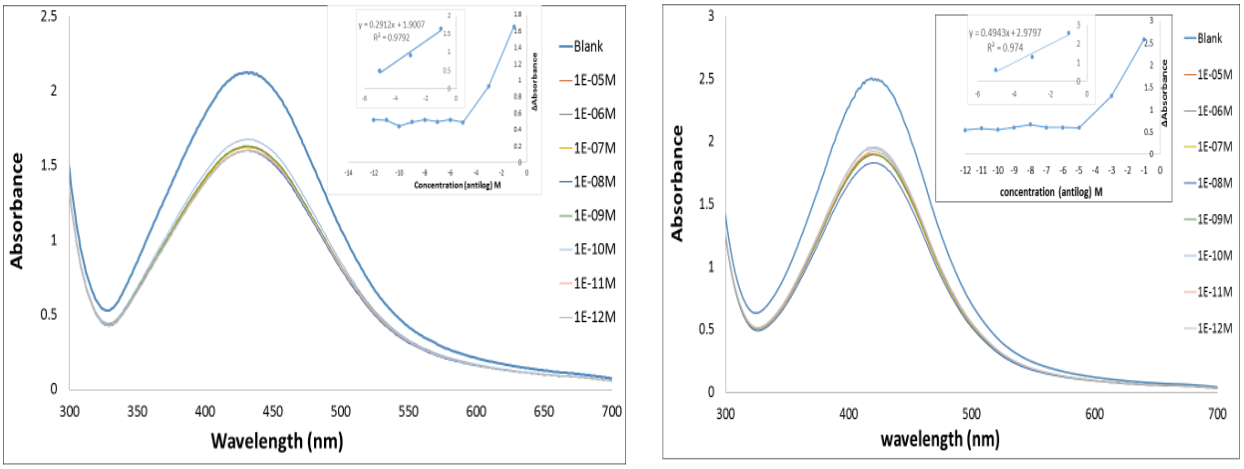


Figure 7. Absorption spectra of (A) Maltose and (B) dextrose reduced Ag-NPs after the addition of 10^{-3} M metal ions (inset: colorimetric response; From far left: Blank, Hg^{2+}, Pb^{2+}, Co^{2+}, Mg^{2+}, Mn^{2+}, Ca^{2+}, Li^{+}, Ba^{2+}, K^{+}, Cr^{3+} and Fe^{2+}.

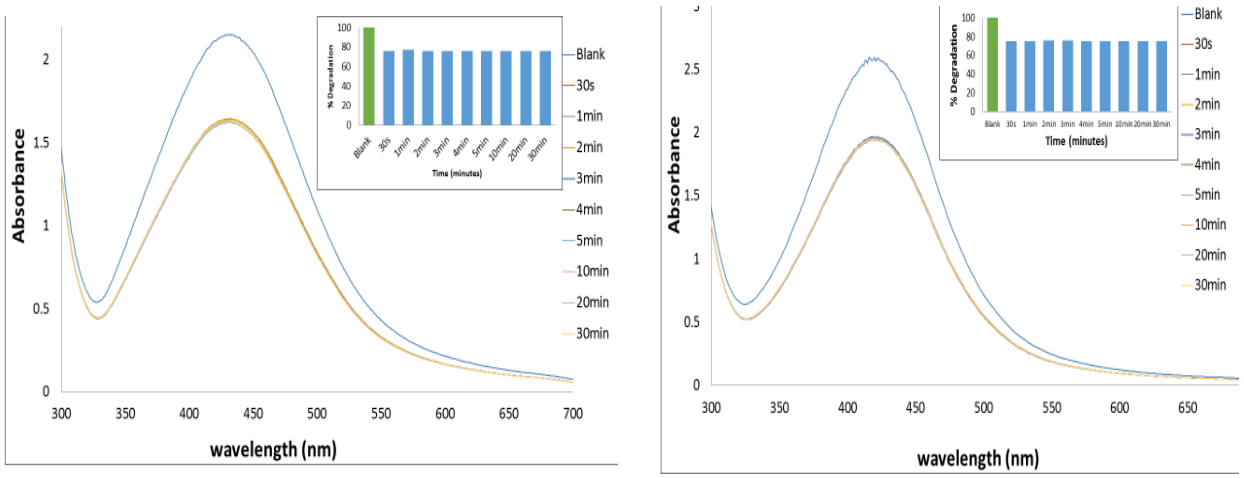
3.3. Ag-NPs sensing of Hg^{2+} ion at varied concentrations and reaction times

The study on the metal ion sensing efficacy of Ag-NPs revealed that both maltose and dextrose-reduced Ag-NPs were selective to Hg^{2+} ions. Thus, Ag-NPs were further studied for Hg^{2+} ion sensing at varied concentrations and reaction times. Figure 8 shows, the sensitivity of both maltose and dextrose reduced Ag-NPs to Hg^{2+} ion at concentration between 10^{-5} M and 10^{-12} M after 30 s of reaction time. The absorption spectra show decrease in the SPR peak intensity for all the concentrations compared to the blank. This indicates the sensitivity of the Ag-NPs to Hg^{2+} ion even at lower concentrations. However, there was no significant change in the sensitivity of the two Ag-NPs solutions to the Hg^{2+} ion after 10^{-5} M. A linear plot with R^2 value of 0.9792 and 0.9740 was observed respectively for maltose and dextrose reduced Ag-NPs over a range of 10^{-1} to 10^{-5} M (Fig.8 inlet). This suggests that the plot can be used to estimate Hg^{2+} ion concentration within this range. The change in the SPR peak intensity at different reaction time after the addition of 10^{-5} M Hg^{2+} ion is shown in Fig. 9. The change in the SPR peak intensity is similar for both solution throughout the different reaction time. Furthermore, there was no significant shift in the SPR peak intensity (% degradation) after 30 s and for the rest of the reaction time (Fig. 9 inset). This shows that the Ag-NPs can be potential Hg^{2+} ion sensors within a short reaction time of 30 s.



A B

Figure 8. Absorption spectra of (A) maltose and (B) dextrose- reduced Ag-NPs after addition of various concentrations of Hg^{2+} ions. (Inlet: Linear plot of change in absorbance at different concentrations)



A B

Figure 9. Absorption spectra of (A) maltose and (B) dextrose-reduced Ag-NPs after the addition of Hg^{2+} ion at different reaction times. (inset % degradation at different reaction time)

4. CONCLUSION

Completely green synthesized dextrose and maltose-reduced silver nanoparticles using gelatin as a capping agent were reported. The formation of Ag-NPs was confirmed by UV-Visible spectroscopy, TEM, DLS analysis and FTIR spectroscopy. The average particle size diameter were 11.88 ± 1 nm and 18.17 ± 1 nm for maltose and dextrose reduced Ag-NPs respectively. In general, dextrose-reduced Ag-NPs proved to be more sensitive to metal ions than the maltose-reduced Ag-NPs at higher metal ion concentrations. Both maltose and dextrose reduced Ag-NPs were found to be sensitive to all the metal ions tested but selective only to Hg^{2+} and Fe^{2+} ions at 0.1 M and only Hg^{2+} ion at 0.001 M and beyond. The sensor reaction showed good sensitivity for Hg^{2+} ions up to 10^{-12} M

with a linear plot over a range of 10^{-1} M to 10^{-5} M. This plot suggests that Hg^{2+} ion can be estimated in a shortest time of 30 s if the concentration is within this range.

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