Redox properties and temperature dependence of silver nanoparticles synthesized using pasteurized cow and goat milk

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ABSTRACT
Nanoparticles (NPs) have a variety of applications in different fields. Green method of NP synthesis is an exciting field and recently has gained more attention. In many green methods, plant extracts are used, and in a few studies, animal milk has been used to synthesize metal NPs. Many studies have aimed to synthesize silver nanoparticles (Ag NP) for agricultural use, however, there are many other applications where green NPs can be used. In this work, we examined the electrochemical behavior of Ag NPs synthesized using cow and goat milk at two different temperatures. Synthesized NPs at temperatures of 25 and 37°C were characterized using UV-Vis spectroscopy, Fourier Transform Infra-Red measurements, dynamic light scattering measurements, scanning electron microscopy, energy dispersive x-ray spectroscopy, and x-ray diffraction spectroscopy. Cyclic voltammetry experiments were performed using two buffer systems: the phosphate, and Tris-HCl, at pH = 7.4. The results showed that the average size of Ag NPs made using goat milk does not change significantly with temperature compared to Ag NPs made using cow milk. Here we demonstrate that Ag NPs synthesized display redox properties that have potential to use in applications relevant to other fields such as biosensing, electrocatalysis, and nanoelectronics.

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Introduction
Green synthesis of nanoparticles (NPs) has become the focus of many areas of research in the recent past as this method produces environmentally friendly, and less toxic NPs of varying sizes for many different applications, specifically in biomedical and agricultural applications. Green methods provide the synthesis of NPs of different sizes using different starting materials and various metals (1–5) and silver (Ag) is the most commonly used metal to prepare eco-friendly nanoparticles (6–8). In addition to Ag, researchers have also used other metals such as platinum, copper, zinc, and iron to prepare nano-size less toxic NPs (9,10). Silver ions have a reduction potential of 0.22 V. In the process of preparing the Ag NPs, the silver ions are reduced to silver and it result in a color change due to the presence of the Surface Plasmon Resonance (SPR). This phenomenon is a collective oscillation of free electrons of the metal nanoparticles in resonance with the frequency of light wave interactions and the band appearing in the
visible region (1). Green synthesis of Ag NPs has shown antibacterial, antifungal, and antimicrobial properties (10–12). The metal ion reduction in green synthesis methods occurs by proteins, amino acids, and many other biological molecules. In many green Ag NP syntheses, plant extracts have been widely used (2,10,13–15) and have looked at the antioxidant, and antimicrobial properties. A recent review discusses the use of various extracts to prepare Ag NPs and in a few studies, milk was used to prepare Ag NPs and investigated their antibacterial properties (12,16–18). Of the studies involving milk, Ihum et al. (19), has used goat milk to prepare Ag NPs and investigated antibacterial properties (19). Further, antifungal activity and multidrug resistivity have been investigated using Ag NPs derived using cow milk (11,20). In addition to these two types of milk, the incorporation of Camel milk in Ag NPs was investigated to look for antibacterial properties (17). In the studies where cow milk Ag NPs are synthesized, the size variations were 30–90 nm when the experiment was carried out at room temperature, and when the experiment is performed at 37°C, the size reported is 20–200 nm (11,12,17,20). In the NP preparation using goat milk, the size reported is 10–100 nm, with the preparation made at 30°C (19). In addition to the temperature variations, the time and the shaker speeds have been different. In all these reported studies, the goals of the investigations have been the use of Ag NPs derived from either cow or goat milk to investigate the antibacterial and/or antifungal activities as plant disease control is vital to the agricultural industry. In addition to the agriculture, there is great interest of eco-friendly NPs in different fields such as biosensing, electrocatalysis, nanoelectronics, water quality assessment, and toxicology studies (21,22). The reactivity of metal complexes can be monitored using electron transfer processes. Electrochemistry is a valuable method in the determination of the electrochemical properties of metal nanoparticles and Cyclic Voltammetry (CV) is used to study the reaction mechanism where electron transfer is involved. Previous work suggests that the size of the NPs plays a critical role in the electrochemical behavior of Ag NPs (21). In that work, commercially available Ag NPs with narrow size distributions have been used (21). Even though more work is emerging using green methods recently, the focus of the majority of those work has been on nanoparticle preparation and not much attention is given to the electron transfer process associated with these silver complexes formed.

Milk has long been seen as a healthy drink because it is high in a range of nutrients and contains all the essential amino acids. It is a readily available product compared to plant extracts, and studies have already demonstrated that it can be used to prepare Ag NPs. The proteins present in milk are thought to be responsible for reducing the Ag ions (11). In addition to the antifungal and antibacterial properties, if milk NPs demonstrate electrochemical behavior, this will lead to an eco-friendlier and pollution-free NP system that has the potential to be used in other applications. The two most common animal milk available in the market are cow and goat milk. Of the two types of milk, goat milk is a better source of protein and contains less sugar and more calcium, potassium, vitamins B6 and A. It is also reported that it has fewer allergic proteins and easily digestible than cow milk (23). In this work, we used pasteurized cow and goat milk available in the supermarket. We prepared the NPs at two different temperatures to examine the temperature dependence on the average size distribution and study the electrochemical properties of the milk-derived NP systems, which have not been investigated previously. In the electrochemical detection of NPs, we immobilized the NPs on the electrode surface. We used two buffers, 50 mM phosphate buffer and Tris- HCl buffer of pH = 7.4, to observe any electrochemical changes associated with the particle sizes and the buffer conditions (21).

Materials and methods

Materials and instrumentation

Silver nitrate was purchased from Sigma Aldrich (St. Louis, MO), and pasteurized cow (Borden Vitamin D Whole Milk Grade A from Borden dairy company, Dallas, TX) and goat milk (Meyenberg- Goat Milk, Meyenberg, Turlock, CA) was purchased from local stores in TX. A BT Lab system shaker, Jasco V-770 spectrophotometer, Thermo Fisher Scientific Nicolet iS5 FTIR Spectrometer, JEOL JSM-6010LA scanning electron microscope, Zetasi-zer Nano ZS (Malvern Instruments, UK) instrument, Bruker Endeavor spectrometer and a BASI C3 cell stand Model serial # C3 1532S cyclic voltameter was used in the characterization studies.

Synthesis of silver nanoparticles

Cow Ag NPs were prepared as previously described (11,12) with minor modifications. In brief, cow Ag NPs were prepared by mixing 4 ml of pasteurized cow milk mixed with 96 ml of 1 mM silver nitrate solution. The resulting mixture was incubated for 72 h in a shaking incubator at 120 rpm, 37°C, and 25°C. A similar procedure was used to prepare the Ag NPs from pasteurized goat milk. The reduction of the silver ions was monitored by the change in color from milky white to brown. The resultant mixtures were centrifuged at 15,000 rpm for
30 min, and the pellet was washed twice with distilled water and 80% (v/v) ethanol. The pellets were then separated, lyophilized, and collected for further analysis.

**Ultra violet (UV)-visible spectroscopic analysis**

The formation of Ag NPs was initially confirmed visually with the color changes observed between the flask containing the milk with silver and the respective controls. Further confirmation was obtained using a UV-Visible spectrometer. Herein, 2 ml of the diluted nanoparticle suspension were placed in a 1 cm quartz cuvette, and the spectrum was recorded in the range from 300-700 nm. The blank consisted of a water sample immersed in a 1 cm quartz cuvette and was automatically subtracted from the recorded spectra.

**Fourier transform infrared spectroscopy (FTIR) measurements**

To compare the interactions of biomolecules with Ag NPs of pasteurized goat and cow milk, we recorded the FTIR spectra of the synthesized Ag NPs using an FTIR spectrometer with Omnic FTIR software. The IR spectra were recorded in the range 400-4000 cm⁻¹. The samples were directly applied onto the diamond crystal, and the spectra were recorded using the Attenuated Total reflection method.

**Scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), and X-ray diffraction experiments (XRD)**

SEM and EDS analyses were performed using a scanning electron microscope and In TouchScope software. The backscattered electron images were collected using an accelerating voltage of 10kV and a load current ~ 90 µA with a working distance of 9 mm. EDS spectra were collected at a magnification of 2000X and 4000X, and the analyzed area was 0.15 mm² (110 µm × 135 µm). Qualitative and quantification elemental composition was performed with the characteristic x-ray using a silicon-drift detector. The semi-quantification is based on the theoretical correction of the ZAF (Z-atomic number, A-absorption, and F-fluorescent excitation) effect. XRD experiments were performed using wave length = 1.540598 Å, with 40 kV, 25 mA source, and scan type 2θ.

**Size measurements using zetasizer**

The particle size and the polydispersity index of the cow and goat Ag NPs were measured using the Zetasizer nano instrument at 25°C using dynamic light scattering. Herein Ag NPs of milk are suspended in distilled water (polydispersity index 1.33), and the measurements taken using plastic cuvettes (Sarstedt) with 10 mm optical path length with water as the reference. The measurement was repeated three times within a minimum of twelve runs for each measurement (24).

**Cyclic voltammetry studies**

The electrochemical potential experiments were performed using a cyclic voltammeter. The different potential ranges are established based on the type of analyte at the scan rate of 100 mVs⁻¹ and the current of 10 mA. The Carbon, Silver, and platinum wires were the electrodes that used to be categorized as working, reference, and counter electrodes (25). The experiments performed on the silver nanoparticles prepared at 25° and 37°C from pasteurized cow and goat milk. The electrochemical measurements were made in two different buffers, namely the 50 mM phosphate buffer (pH = 7.4) and 50 mM Tris-HCl buffer (pH = 7.4).

**Results and discussion**

**Cow and goat milk**

Cow and goat milk have a long history of consumption by humans and many studies exist in investigating the compositions of the two types of milk (26–30). The main components in milk are water, fat, lactose, whey proteins and minerals and the composition vary depending on the source of origin. The comparison of the ingredients present in the two types of milk are shown in Table 1. Prosser (26), summarizes the average composition, protein composition, amino acids, and other important constituents in both cow and goat milk. A comparison

| Table 1. Comparison of the ingredients present in cow and goat milk. |
|-------------------------------------------------|
| Ingredients (100 ml) | Cow milk | Goat milk |
|---------------------|----------|-----------|
| Calories            | 66.67    | 58.33     |
| Total Fat           | 3.33g    | 2.92g     |
| Saturated Fat       | 2.08g    | 1.67g     |
| Trans Fat           | 0        | 0         |
| Polyunsaturated fat | n/a      | 1.04g     |
| Monounsaturated fat | n/a      | 0.42g     |
| Cholesterol         | 35mg     | 25mg      |
| Sodium              | 130mg    | 115mg     |
| Vitamin D           | 2.5mcg   | 3mcg      |
| Iron                | 0.1mg    | 0 mg      |
| Total Carbohydrate  | 5g       | 4.58g     |
| Dietary Fiber       | 0g       | 0g        |
| Total Sugar         | 4.58g    | 4.58g     |
| Protein             | 3.33g    | 3.33g     |
| Calcium             | 125mg    | 125mg     |
| Potassium           | 166.67mg | 175mg     |
| n/a data not available. Data obtained from the milk carton. |
of the fatty acid compositions of both the milk types are described by Wang et al (27). As several detailed studies on characterizations are available we did not perform any characterizations of the two milk types.

**UV-visible and FTIR characterization of silver nanoparticles**

Ultraviolet–visible spectroscopy was performed of the Ag NPs to investigate the presence of the nanoparticles at the two different temperatures studied. This technique is an effective way to demonstrate the existence of nanostructures. The samples were scanned from 200 to 700 nm wavelength range, and all samples showed peak maxima around 430 nm, indicating the presence of Ag NPs (12,19), as shown in Figure 1. The observed peak maxima were not very sharp and we did not observe any significant shift with the change in the type of the milk or the temperature. Shifting of absorption is expected based on the size and the shape of the metal (31,32). Our results indicate that the geometrical parameters of metal remain similar in all preparations (31–34). In order to identify the functional groups, present in milk that are responsible for reducing silver ions to silver FTIR spectroscopy was used. This method provides the details of the vibrational frequencies of different molecules present in milk that

![UV-Vis absorption spectra of silver nanoparticles synthesized by cow milk (solid line) and goat milk (dashed line). The upper panel (A) represent data for silver nanoparticles synthesized at 25°C while the bottom panel (B) represent data obtained at 37°C.](image-url)
are involved in the Ag NP preparations. Figure 2 displays the FTIR spectra for Ag NPs synthesized from cow and goat milk. The spectra were recorded in the range of 600-4000 cm\(^{-1}\). In agreement with previous studies, we also observe peaks corresponding to C–H stretching, O-H stretching, C–O stretching, C–N stretching, N-O stretching,

**Figure 2.** Fourier transform infrared (FTIR) spectrum of silver nanoparticles synthesized using cow (CW) and goat (GT) milk at temperatures of 25°C (A and B) and 37°C (C and D).

| Absorption range (cm\(^{-1}\)) | Group                        | Compound Class     | CW25°C    | CW37°C    | GT25°C    | GT37°C    |
|-------------------------------|------------------------------|--------------------|-----------|-----------|-----------|-----------|
| 3293–3274                    | O-H Stretching               | Carboxylic Acid/ Alcohol | 3293.57   | 3290.61   | 3282.91   | 3274.16   |
| 2916–2924                    | C-H Stretching               | Alkane             | 2916.54   | 2921.17   | 2922.84   | 2923.09   |
| 2848–2853                    | C-H Stretching               | Alkane             | 2848.59   | 2851.5    | 2852.38   | 2852.65   |
| 1448–1456                    | C-H Bending                  | Alkane (Methyl)    | 1448.2    | 1455.02   | 1454.02   | 1448.53   |
| 1633–1644                    | C = C Stretching             | Alkene             | 1640.34   | 1643.21   | 1633.56   | 1636.54   |
| 1740–1745                    | C-H Bending                  | Aromatic Compound  | 1740.89   | 1743.46   | 1744.46   | 1743.61   |
| 1533–1540                    | N-O Stretching               | Nitro Compound     | 1539.86   | 1536.90   | 1537.53   | 1533.89   |
| 1378–1396                    | O-H Bending                  | Alcohol            | 1390.52   | 1378.55   | 1392.55   | 1395.49   |
| 1235–1238                    | C-N Stretching               | Amine              | 1235.61   | 1237.05   | 1236.16   | 1237.24   |
| 1152–1161                    | C-N Stretching C-O Stretching| Amine; Tertiary Alcohol | 1152.26   | 1161.08   | 1157.23   | 1154.70   |
| 1070–1098                    | C-N Stretching               | Amine              | 1070.75   | 1097.62   | 1093.36   | 1084.06   |
| 643–668                      | C = C Stretching             | Alkene             | 643.99    | 656.04    | 667.56    | 662.02    |
O-H bending, C–H bending, and C = C bending. The functional groups indicate the presence of alcohol, carboxylic acids, amines, and aromatic compounds (phenols) in the Ag NPs. The table representing the wavenumbers and the corresponding vibrational modes are given in Table 2. The FTIR spectra show that cow and goat milk proteins containing these functional groups are acting as the capping and stabilization biomolecules in the synthesis of the Ag NPs \((12,19,23)\). Small shifts in the intensities and frequencies were observed in the four different preparations depending on the type of the milk, and the temperature and the data are shown in Figure 2 and Table 2. Samples at 37°C have shorter wavenumbers compared to 25°C, and goat Ag NP have shorter wave numbers than cow Ag NPs. In cow milk preparations, an increase in temperature from 25°C to 37°C, the wavenumbers shifted to shorter wave numbers.

**SEM-EDS, XRD studies and size measurements**

The synthesized nanoparticles for cow and goat milk generated strong energy dispersion when using EDS (Figure 3) and SEM (Figure 4). The spectrum provides quantitative information of the Ag NPs synthesized. Quantitative data of the Ag NPs synthesized in both samples exhibit strong absorption peaks for silver between the ranges of 2.75 and 3.25 keV (Figure 3). The data presented below demonstrate the presence of silver as described previously \((12)\). The peaks obtained around 3.0 keV are due to the absorption from metallic silver surface plasmon resonance \((11,12)\). EDS data showed the presence of other elements carbon (C), oxygen (O), phosphorous (P), aluminum (Al), chlorine (Cl), and calcium (Ca), and the percentages of these elements are shown in Table 3, and are consistent with the results reported by Athreya et al. \((12)\) where silver nanoparticles were synthesized at 37°C using cow milk. As previously reported, the trace elements present may also be responsible for the protein capping over the synthesized nanoparticles \((12)\). The surface morphology of the Ag NPs was viewed at magnifications at 2,000x and 4000x. They are spherical and globular in shape \((35,36)\). The SEM image also showed the aggregation of the Ag NPs. We have observed that the particle tends to be polydisperse. Figures 4(a and c) show that more NPs are present in goat milk than in cow milk at 25°C. On the other hand, more Ag NPs were visible on the cow milk sample than in the goat milk sample at 37°C as seen in Figures 4(b and d). Most of the NPs formed showed a tendency to congregate as in sample Figures 4(b and c) and are more sparsely as in 4a and 4d. Possible causes are lipids and proteins surrounding the Ag NPs, as shown in
Figure 4. XRD patterns of the synthesized NPs are shown in Figure 5. The reflection peaks appear broader indicating the formation of Ag NPs. All preparations showed the same diffraction peaks at 2θ. The four peaks at 38.2°, 46.3°, 67.6° and 76.8° can be indexed on the basis of the face centered cubic (fcc) silver structure with the corresponding diffraction peaks of (111), (200), (220) and (311), planes. These characteristics were compared to Joint Commission of Powder Diffraction Standards (JCPDS) No 84–0713 and 04-0783. The results obtained here are similar to previously reported results for green Ag NPs (37–41). The unassigned peaks at 27.9°, 32.3°, 54.9° and 57.6° could be attributed to biomass capping of Ag NPs and suggest the crystallization of the bioorganic phase occurring on the surface of the Ag NPs (38–41). Figures 6 show the size distribution patterns obtained using dynamic light scattering measurements. For the cow Ag NPs, the average diameter was found to be 87 and 138 nm at 25°C and 37°C respectively while that for goat Ag NPs were 165 and 180 nm range at 25°C and 37°C. Previous sizes reported for cow Ag NPs by Lee et al., and Hegazi et al. (11,17) was varying from 30 to 90 nm, when the experiment carried out at room temperature for 8 h. Athreya et al. (12) reported the sizes to be 20–200 nm when the experiment was performed at 37°C for 72 h. However, in none of the previous reports, the average size measurements were done using dynamic light scattering experiments. Herein, we observe a moderate size increase in the cow Ag NPs when the experimental temperatures are increased. Only one previous report is available for the synthesis of goat Ag

Table 3. Mass percent of cow (CW) and goat (GT) milk AgNPs at 25°C and 37°C.

| Chemical formula | CW 25°C | CW 37°C | GO 25°C | GO 37°C |
|------------------|---------|---------|---------|---------|
| C                | 65.53   | 61.84   | 64.77   | 67.87   |
| O                | 21.58   | 20.44   | 24.21   | 21.85   |
| P                | 1.2     | 1.24    | 1.18    |         |
| Al               | 1.83    | 0.96    |         |         |
| Cl               | 1.93    | 2.49    | 1.06    | 1.49    |
| Ca               | 2.61    | 1.61    | 1.28    | 1.59    |
| Ag               | 7.15    | 11.79   | 6.48    | 6.01    |
| Total            | 100     | 100     | 100     | 100     |

Acquisition Condition
Real Time (s) 102.35 103.15 102.63 103.00
Dead Time 2.00% 4.00% 3.00% 3.00%
Count Rate (CPS) 8193.00 10913.00 9637.00 10907.00

In all cases the instrument, process time, and live time were the same.
NPs where the size reported to be 10–100 nm when the experiment was carried out at 30°C and for 24 h (19). Our results show higher average diameters and relatively stable goat milk NPs as compared to the cow milk NPs. Further, with the preparation temperature changes, the changes in size observed for the goat milk NPs were relatively small.

Redox properties of silver nanoparticles of goat and cow milk

Electron transfer properties of both cow and goat milk Ag NPs were investigated using two-buffer systems and used to carry out the CV studies. To ensure silver oxidation is easily obtained, all experiments were performed with Ag NP modified electrodes with similar silver coverages to ensure the ease of the silver oxidation peak potential using cyclic voltammetry (21,42). The results shown in Figure 7 show the potential windows for both types of NPs in the two different buffer systems (21). The starting and switching potentials for the Ag NPs made at 37°C were similar in all cases except for cow NPs in phosphate buffer. For particles made at 25°C, the starting potentials were the same for all, but the switching potentials were different for all cow and goat particles. The lower values of the switching potentials of the cow particles may be attributed to the smaller size of the cow NPs synthesized at

Figure 5. X-ray diffraction (XRD) pattern of AgNPs synthesized using cow (CW) and goat (GT) milk at 25°C (A-CW and B-GT) and 37°C (C-CW and D-GT).
25°C. The responses observed in all cases were different, and in some cases, small oxidation and reduction peaks were observed. Overall, here we demonstrate for the first time that Ag NPs synthesized using cow and goat milk show electron transfer properties and may be useful in using these for potential applications such as biosensing, electrocatalysis, and nanoelectronics. The CV data shows that the electrode potential of the goat milk does not offer a significant variation with the choice of buffer and the temperature at which the preparation is made. However, cow milk preparation showed a considerable change in the selection of buffer at one temperature. In contrast, the other preparation had a more negligible effect on the choice of the buffer. The

Figure 6. Size distribution intensity of Cow (CW) and goat (GT) milk AgNPs at 25°C (A-CW 25 and B-GT 25) and 37°C (C-CW 37 and D-GT 37) obtained using dynamic light scattering measurements. The plots show the average size of the different AgNPs.
different electrochemical stabilizing effects can account for this behavior excreted by the protein molecules on the Ag NPs. The oxidative peak of silver was visible in all voltammograms, with the peak size varying on the preparation and the choice of the buffer and may be due to the particle size.

**Figure 7.** A comparison of cyclic voltammograms of AgNPs obtained using cow (CW) and goat (GT) milk at different temperatures and in different buffers. The upper panel represents the overlapped cyclic voltammograms obtained at 25°C for silver nanoparticles of cow (solid line) and goat (dashed line) and A were obtained using phosphate buffer while B obtained using 50 mM Tris-HCl buffer. The lower panel represents the overlapped cyclic voltammograms obtained at 37°C for silver nanoparticles of cow (solid line) and goat (dashed line) and C were obtained using phosphate buffer while D obtained using 50 mM Tris-HCl buffer.
Conclusion
In conclusion, this study examined the electrochemical properties of Ag NPs synthesized using cow and goat milk. The preparation method of the Ag NP system was straightforward and inexpensive and was carried out at different temperatures. Results indicate that depending on the type of animal milk used to synthesize the NP’s, the size can vary and the electrochemical properties. The charges of the proteins involved in the NP synthesis make it possible for these NPs to be used in fields such as biosensing, electrocatalysis, nanoelectronics, water quality assessment, and toxicology studies in addition to agricultural applications.

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References

[1] Firdhouse, M.J.; Lalitha, P. Biosynthesis of Silver Nanoparticles and Its Applications. J. Nanotechnology 2015, 2015.
[2] Selvan, D.A.; Mahendiran, D.; Kumar, R.S.; Rahiman, A.K. Garlic, Green tea and Turmeric Extracts-Mediated Green Synthesis of Silver Nanoparticles: Phytochemical, Antioxidant and in Vitro Cytotoxicity Studies. J. Photochem. Photobiol. B 2018, 180, 243–252.
[3] Mahiuddin, M.; Saha, P.; Ochhai, B. Green Synthesis and Catalytic Activity of Silver Nanoparticles Based on Piper Chaba Stem Extracts. Nanomaterials 2020, 10, 1777.
[4] Nadaroglu, H.; Gungor, A.A.; Ince, S.; Babagil, A. Green Synthesis and Characterisation of Platinum Nanoparticles Using Quail egg Yolk. Spectrochim. Acta A: Mol. Biomol. Spectrosc. 2017, 172, 43–47.
[5] Pan, Z.; Lin, Y.; Sarkar, B.; Owens, G.; Chen, Z. Green Synthesis of Iron Nanoparticles Using red Peanut Skin Extract: Synthesis Mechanism, Characterization and Effect of Conditions on Chromium Removal. J. Colloid Interface Sci 2020, 558, 106–114.
[6] Siddiqi, K.S.; Husen, A.; Rao, R.A.K. A Review on Biosynthesis of Silver Nanoparticles and Their Biocidal Properties. J. Nanobiotechnology 2018, 16 (1), 14.
[7] Nidkau, M.; Noah, N.M.; Andala, D.M.; Masika, E. Green Synthesis and Characterization of Silver Nanoparticles Using Citrullus Lanatus Fruit Rind Extract. Int. J. Anal. Chem 2017, 2017.
[8] Pandey, S.; De Klerk, C.; Kim, J.; Kang, M.; Fosso-Kankeu, E. Eco Friendly Approach for Synthesis, Characterization and Biological Activities of Milk Protein Stabilized Silver Nanoparticles. Polymers. (Basel) 2020, 12, 1418.
[9] Gholami-Shabani, M.; Shams-Ghahfarokhi, M.; Gholami-Shabani, Z.; Akbarzadeh, A.; Riazi, G.; Razzaghi-Abayneh, M. Biogenic Approach Using Sheep Milk for the Synthesis of Platinum Nanoparticles: The Role of Milk Protein in Platinum Reduction and Stabilization. Int. J. NanoSci. Nanotechnol 2016, 12 (4), 199–206.
[10] El-Refaei, A.A.; Ghoniem, G.A.; El-Khateeb, A.Y.; Hassaan, M.M. Eco-friendly Synthesis of Metal Nanoparticles Using Ginger and Garlic Extracts as Biocompatible Novel Antioxidant and Antimicrobial Agents. J. Nanostruct. Chem 2018, 8, 71–81.
[11] Lee, K.; Park, S.; Govarthanan, M.; Hwang, P.; Seo, Y.; Cho, M.; Lee, W.; Lee, J.; Kamala-Kannan, S.; Oh, B. Synthesis of Silver Nanoparticles Using cow Milk and Their Antifungal Activity Against Phytopathogens. Mater. Lett 2013, 105, 128–131.
[12] Athreya, A.G.; Shareef, M.I.; Gopinath, S.M. Antibacterial Activity of Silver Nanoparticles Isolated from Cow’s Milk, Hen’s Egg White and Lysozyme: A Comparative Study. Arab J. Sci. Eng 2019, 44, 6231–6240.
[13] Makarov, V.V.; Love, A.J.; Sinitsyna, O.V.; Makarova, S.S.; Yaminsky, I.V.; Taliansky, M.E.; Kalinina, N.O. Green Nanotechnologies: Synthesis of Metal Nanoparticles Using Plants. Acta Naturae. 2014, 6 (1), 35–44.
[14] Netala, V.R.; Kotakadi, V.S.; Domdi, L.; Gaddam, S.A.V.; Bobbu, P.; Venkata, S.K.; Ghosh, S.B.; Tartte, V. Biogenic Silver Nanoparticles: Efficient and Effective Antifungal Agents. Appl. Nanosci 2016, 6, 475–484.
[15] Carson, L.; Bandara, S.; Joseph, M.; Green, T.; Grady, T.; Osuji, G.; Woldeisenbet, S. Green Synthesis of Silver Nanoparticles with Antimicrobial Properties Using Phylica-Dulcis Plant Extract. Foodborne Pathog. Dis 2020, 8, 504–511.
[16] Ijaz, M.; Zafar, M.; Iqbal, T. Green Synthesis of Silver Nanoparticles by Using Various Extracts: A Review. Inorg. Nano-Met. Chem 2021, 51, 744–755.
[17] Hegazi, A.; Elshazly, E.H.; Abdou, A.M.; Abdou, A.F.; Allah, F.A.; Abdel-Rahman, E.H. Potential Antibacterial Properties of Silver Nanoparticles Conjugated with Cow and Camel Milks. Glob. Vet 2014, 12 (6), 745–749.
[18] Han, S.; Zhang, H.; Xie, Y.; Liu, L.; Shan, C.; Li, X.; Liu, W.; Tang, Y. Application of cow Milk-Derived Carbon Dots/Ag NPs Composite as the Antibacterial Agent. Appl. Surf. Sci. 2015, 326, 368–373.
[19] Ihum, T.A.; Iheukwumere, C.C.; Ogbonna, I.; Gberikon, G.M. Antimicrobial Activity of Silver Nanoparticles...
[20] Athreya, A.G.; Shareef, M.J.; Gopinath, S.M. Silver Nanoparticles from Cow’s Milk to Combat Multidrug-Resistant Gram-Negative Bacteria from Clinical Isolates. *Proc. Natl. Acad. Sci., India, Sect. B Biol. Sci.* **2020**, *90*, 863–871.

[21] Giovanni, M.; Pumera, M. Size Dependent Electrochemical Behavior of Silver Nanoparticles with Sizes of 10, 20, 40, 80 and 107 nm. *Electroanalysis* **2012**, *24* (3), 615–617.

[22] Chen, W.; Wang, H.; Tang, H.; Yang, C.; Li, Y. Unique Voltammetry of Silver Nanoparticles: From Single Particle to Aggregates. *Anal. Chem.* **2019**, *91* (22), 14188–14191.

[23] Roncada, P.; Gaviraghi, A.; Liberatori, S.; Canas, B.; Bini, L.; Greppi, G.F. Identification of Caseins in Goat Milk. *Proteomics* **2002**, *2* (6), 723–726.

[24] Saravanan, T.; Anandan, P.; Shanmugam, M.; Jayakumari, T.; Arivanandhan, M.; Azhagurajan, M.; Hayakawa, Y.; Jayavel, R. Impact of Graphene on the Enhancement of Electrochemical and Photocatalytic Performance of Gd2O3 - Graphene Nanocomposites. *Solid State Sci.* **2018**, *83*, 171–180.

[25] Collard, K.M.; McCormick, D.P. A Nutritional Comparison of Cow’s Milk and Alternative Milk Products. *Acad. Pediatr.* **2021**, *21* (6), 1067–1069.

[26] Mahumudin, L.; Suharyadi, E.; Utomo, A.B.S.; Abraha, K. Optical Properties of Silver Nanoparticles for Surface Plasmon Resonance (SPR)-Based Biosensor Applications. *J. Mod. Phys.* **2015**, *6*, 1071–1076.

[27] Athreya, A.G.; Shareef, M.J.; Gopinath, S.M. Silver Nanoparticles from Cow’s Milk to Combat Multidrug-Resistant Gram-Negative Bacteria from Clinical Isolates. *Proc. Natl. Acad. Sci., India, Sect. B Biol. Sci.* **2020**, *90*, 863–871.