



NANOCELLULOSE AS A STABILIZING AGENT IN THE SYNTHESIS OF SILVER NANOPARTICLES UNDER TRACE LEVEL TRISODIUM CITRATE

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Abstract

Silver nanoparticles (AgNPs) synthesized in dilute solutions of silver metal precursor and reducing agents are less toxic and safe for diverse applications. In this research, AgNPs which were successfully synthesized at trace level of trisodium citrate and stabilized with cellulose nanoparticles were characterized with FTIR spectroscopy, UV-Vis, x-ray diffraction (XRD) and scanning electron microscopy (SEM). The AgNPs synthesized in the presence of nanocellulose had better surface plasmon resonance and showed lesser aggregation according to the UV and SEM results.

Keywords: Silver nanoparticles, Nanocellulose, Stabilizing, Aggregation

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Classification Number: 2.04

1.0 Introduction

In recent times, Silver nanoparticles (AgNPs) are one of the most commonly used nanomaterials which account for more than 23% of all nano-products (Chouhan 2018). They have good electrical and thermal conductivity, chemical stability, anti-inflammatory, anti-cancer, anti-viral, anti-bacterial, anti-giogenic and anti-fungal, activity (Zhang et al., 2016). This class of nanoparticles is being incorporated into a wide range of consumer products such as washing machines, textiles, disinfectants and filters.

AgNPs can be synthesized using either the chemical reduction synthesis route, the physical synthesis route, the photochemical synthesis route or the biological synthesis route

(El-Nour et al., 2010). Each synthetic route mentioned above has different type of methods of synthesis grouped under it. However, the method of synthesis employed determines the characteristics of the AgNPs that will be obtained in terms of its size and shape. Advantages and disadvantages of these methods varies but with problems such as particle sizes, costs, size distribution, and scalability.

The use of various polymers including carboxymethyl cellulose (Hebeish et al., 2010), chitosan (Venkatesham et al., 2014), cellulose (Mochochoko et al., 2013), starch (Vigneshwaran et al., 2006) and polysaccharide (Huang et al., 2004) as stabilizers during the synthesis of AgNPs has been reported. Among these polymers, the use cellulose as stabilizing agents has advantage of easing the separation of

the NPs for further modification due to the reversible and non-covalent silver nanoparticles-fibre interactions (Mochochoko et al., 2013).

The present study therefore aim to synthesize AgNPs using nanocellulose as stabilizing agent and trace amount of trisodium citrate as reducing agent.

2.0 Experimental

2.1 Synthesis

All chemicals were purchased from BDH Analar England and were used without further purification.

20 g of commercially obtained cotton wool was placed in a round bottom flask. 60ml of 10% NaOH was introduced to it and refluxed for 40 min at 80 °C. The sample was purified with distilled water to remove excess NaOH. Subsequently, 60 mL of 58% H₂SO₄ was then added and again refluxed for 40 min at 60 °C. The sample was bleached, filtered, washed with methanol, freeze dried and homogenized by blending. The AgNPs were synthesized using the Turkevich method. The reduction of the silver was carried out at different conditions according to Table 1 below.

Table 1: Variation of reagents used

Nanocellulose (grams)	0.00	0.05	0.10	0.20
Na ₃ C ₆ H ₅ O ₇ (mol/dm ³)	0.018	0.018	0.018	0.018
AgNO ₃ (mol/dm ³)	0.01	0.01	0.01	0.01

2.2 Characterizations

Beckman Coulter DU 730 UV/Vis spectrophotometer was employed to characterize the AgNPs. FTIR analysis was carried out at the range 4000 - 650 cm⁻¹ to identify the compound and determine functional groups present. Scanning Electron Microscopic (SEM) analysis was carried out to determine the shape and size of the synthesized AgNPs. The diffraction pattern of the products was recorded in the 2θ range of 10 - 55° at ambient temperature, using XRD.

3.0 Results and discussion

In AgNPs, the closeness of conduction and valence band makes it easier for electrons to move freely. These free electrons generate absorption band of surface plasmon resonance when electrons of silver nanoparticles oscillate

in resonance with light (Iravani et al., 2015). From the UV-visible spectra presented in Figure 1, the silver nanoparticles synthesized at very low concentration of trisodium citrate without nanocellulose as a stabilizing agent showed surface plasmon resonance at an absorption peak of 435 nm. Although, AgNPs synthesized using nanocellulose also have absorption peak at same position, however, their absorbance increase with increase in amount of nanocellulose, which indicates increase in amount of AgNPs in solution (Oluwafemi et al., 2013). Moreover, compared to absorption peak of AgNPs synthesized without nanocellulose, the absorption peak of AgNPs synthesized using 0.20 g of nanocellulose is narrow. Such decrease in broadness of SPR peak indicating the decrease in size with narrow size distribution (Dong et al., 2014).

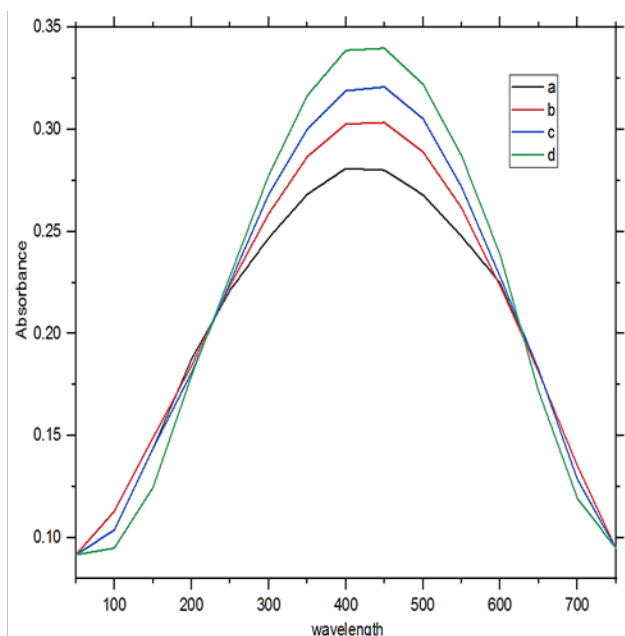


Figure 1: UV-vis spectra of AgNPs synthesized using (a) 0.00 g nanocellulose, 0.018 M trisodium citrate, 0.01M AgNO₃ (b) 0.05 g nanocellulose, 0.018M trisodium citrate, 0.01M AgNO₃ (c) 0.10 g nanocellulose, 0.018M trisodium citrate, 0.01M AgNO₃ (d) 0.20 g nanocellulose, 0.018M trisodium citrate, 0.01M AgNO₃.

FTIR spectra of the synthesized AgNPs with and without nanocellulose stabilization are shown in Figure 2 – 5. FTIR of the synthesized AgNPs without nanocellulose stabilization showed the transmittance peak for AgNPs at 700 cm⁻¹. For the AgNPs synthesized in the presence of 0.05, 0.10 and 0.20 g of nanocellulose, transmittance peaks for the stretch and bend of hydroxyl (O-H), carbonyl (C=O) and glycosidic ether (C-O-C) functional

groups were present (Yuan et al., 2019). The transmittance peaks for hydroxyl group decreases from 3338 to 3332 to 3330 cm⁻¹ for the AgNPs synthesized with 0.05, 0.10 and 0.20g respectively indicating that the quantity of hydroxyl reducing groups consumed is directly proportional to the concentration of silver nanoparticles precursor used. The carbonyl functional group stretching vibration of the three silver nanoparticles stabilized in the presence of nanocellulose also decreased from 1651 to 1630 to 1625 cm⁻¹, while the ether linkage between the glucopyranose unit of the cellulose biopolymer was also seen to vary between 1203 to 1107 cm⁻¹ to confirm the successful synthesis of the stable silver nanoparticles by reduction process. The synthesis of stabilized silver nanoparticles was confirmed by the transmittance band at 663 cm⁻¹ to 654 cm⁻¹ (Noah et al., 2019). The AgNPs obtained in the presence of nanocellulose were more stable than those obtained without cellulose nanoparticles which had their transmittance at 700 cm⁻¹. The lower the wavenumber of the nanoparticle synthesized, the better the stability of the nanoparticles and its surface plasmon resonance effect. The decrease in the transmittance for the hydroxyl and carbonyl groups on the nanocellulose suggests that the O-H groups also participated in the reduction of the silver particles while the van der waal bond (C₆-O-Ag) which result as an interaction between the carbon-6 oxygen atom and the nanosilver formed stabilizes the nanoparticle medium.

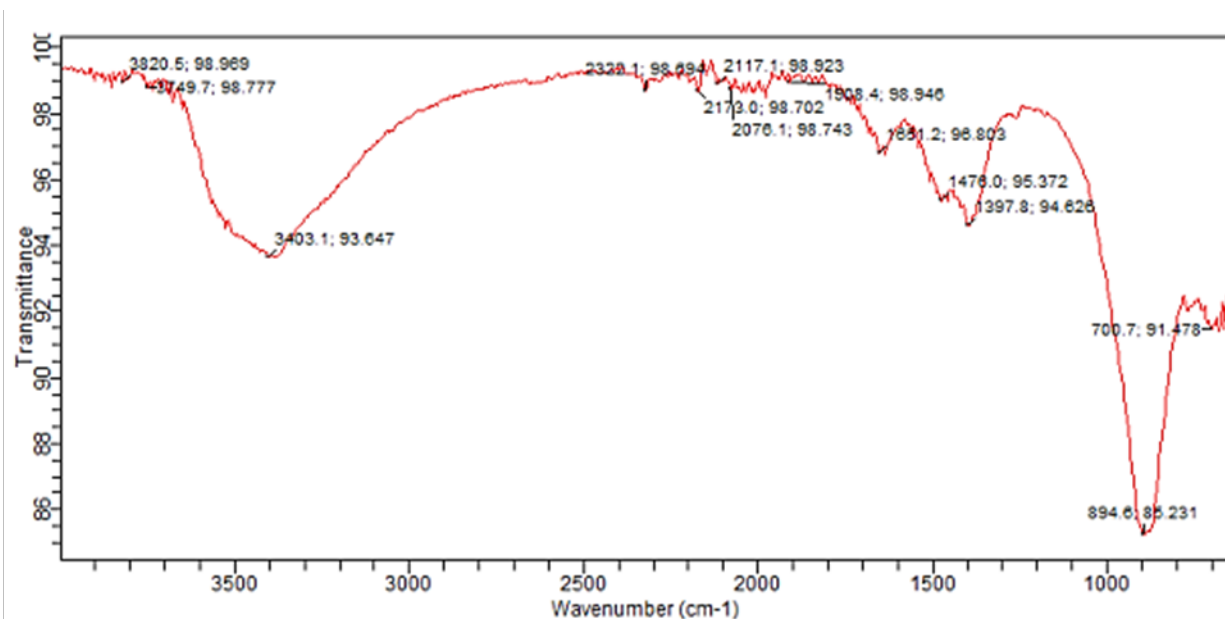


Figure 2: FTIR spectrum of AgNPs synthesized using 0.00 g nanocellulose, 0.018M trisodium citrate and 0.01M AgNO₃.

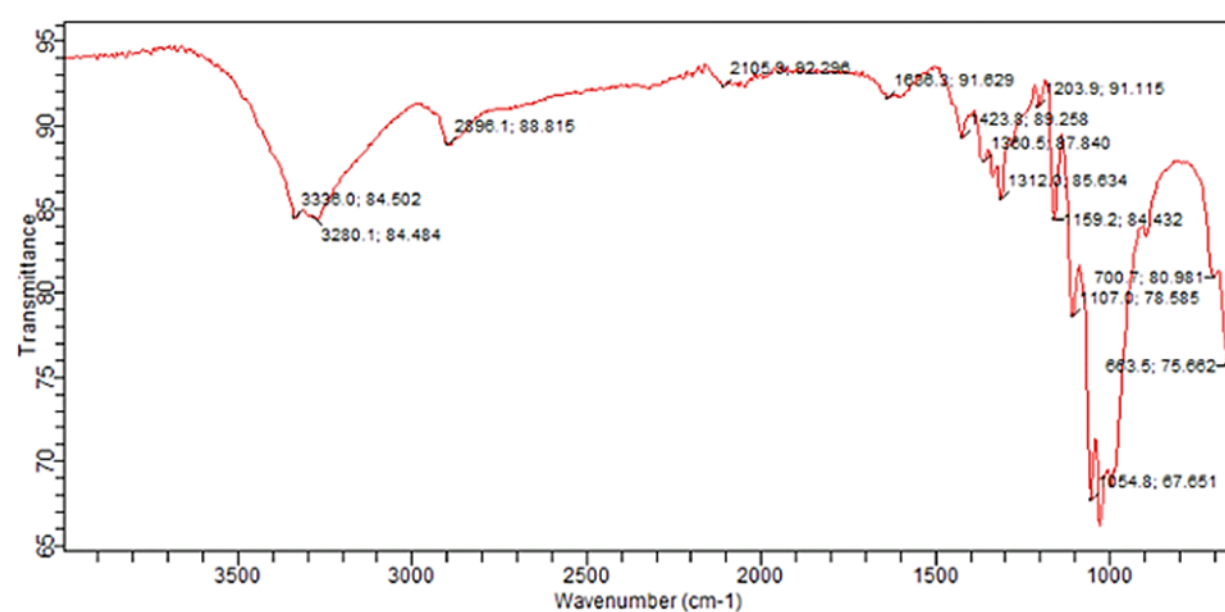


Figure 3: FTIR of spectrum of AgNPs synthesized using 0.05 g nanocellulose, 0.018M trisodium citrate and 0.01M AgNO₃.

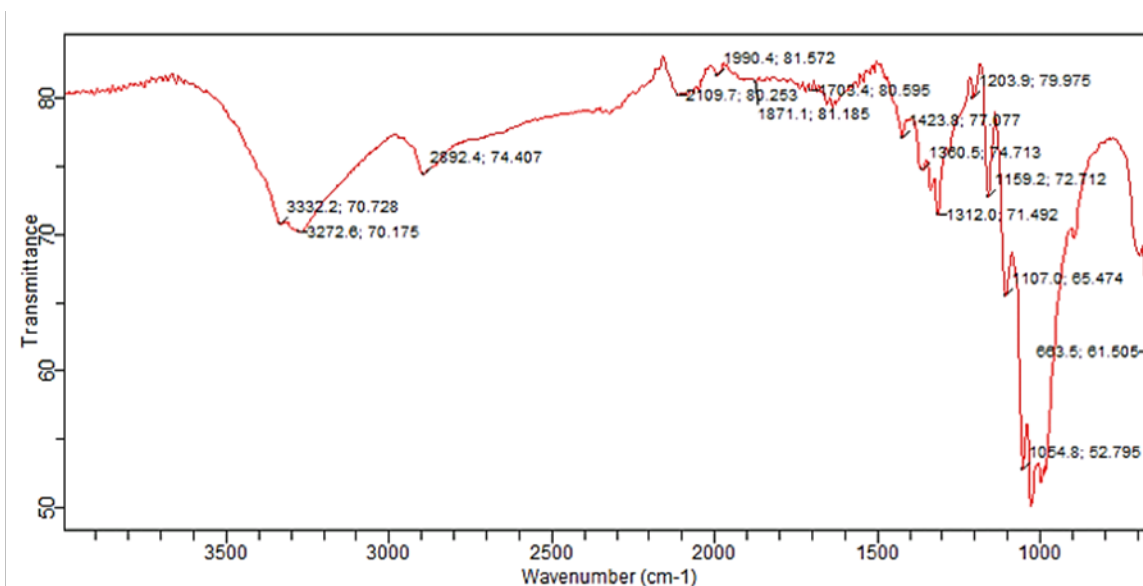


Figure 4: FTIR spectrum of AgNPs synthesized using 0.10 g nanocellulose, 0.018M trisodium citrate and 0.01M AgNO₃.

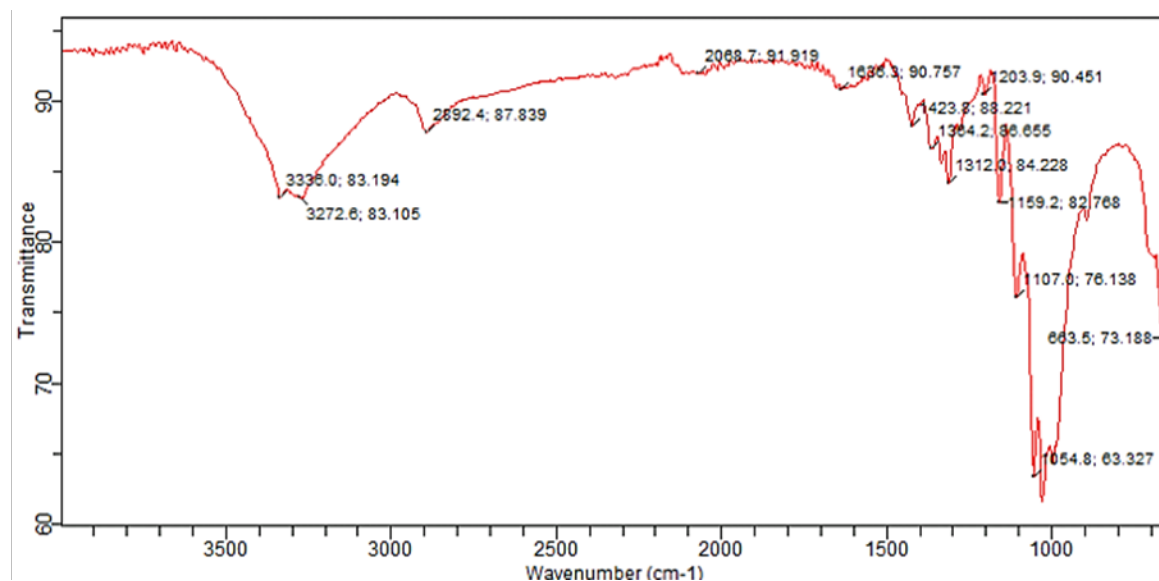


Figure 5: FTIR spectra of AgNPs synthesized using 0.20 g nanocellulose, 0.018M trisodium citrate and 0.01M AgNO₃.

From the SEM images presented in Figure 6, the nanosilver particles obtained without stabilization appeared clumsy and matched together. Therefore, it might be possible that over time, the nanoparticles undergo aggregation and switch from nano level to micro level (Fernando et al., 2019). The silver nanoparticles synthesized in the presence of nanocellulose were finer, well spread and therefore more stable since the high degree of

spread will decrease any tendency for aggregation which can make the particle switch away from their nano state (Fernando et al., 2019). The SEM images also confirmed that the nanosilver particles were not absorbed by the nanocellulose but they were evenly spread on the cylindrical fibres as a result of even charge distribution between the stabilizing fibres and the silver nanoparticles (Ru et al., 2018).

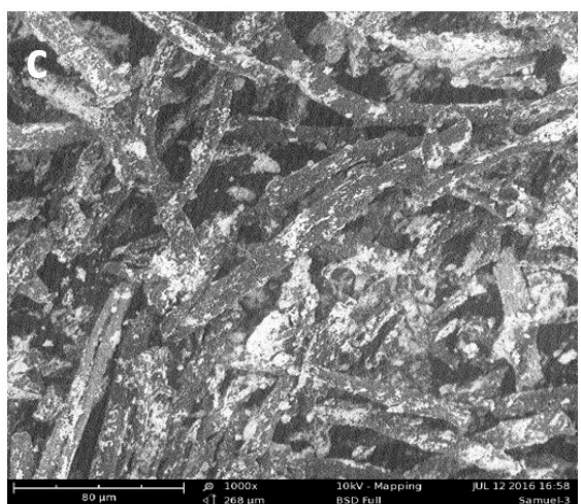
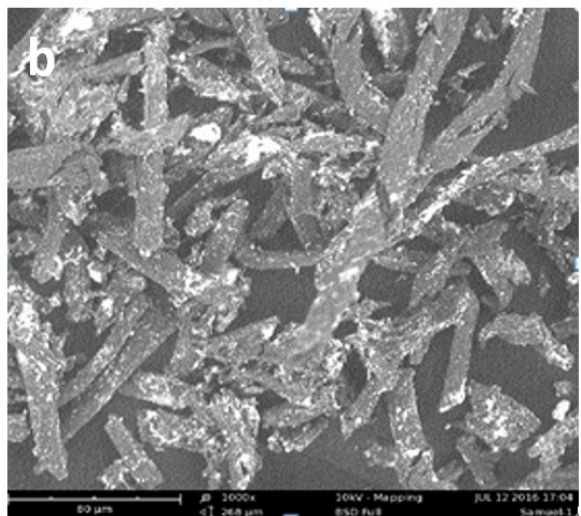
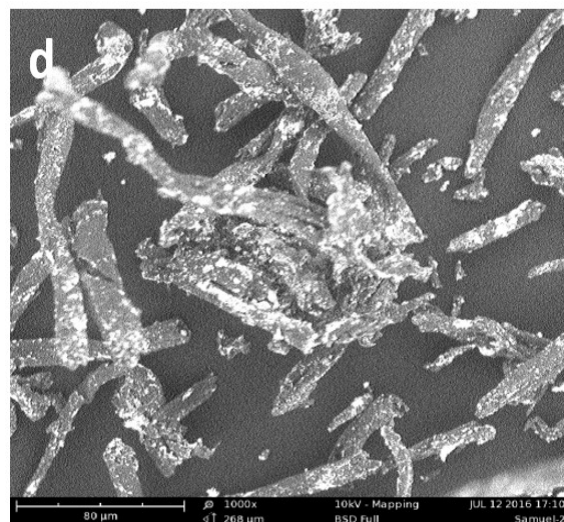
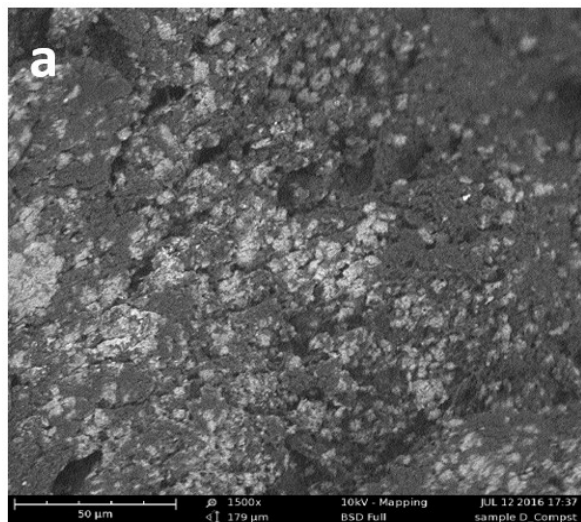


Figure 6: SEM of AgNPs synthesized using (a) 0.00 g nanocellulose, 0.018M trisodium citrate, 0.01M AgNO_3 (b) 0.05 g nanocellulose, 0.018M trisodium citrate, 0.01M AgNO_3 (c) 0.10 g nanocellulose, 0.018 M trisodium citrate, 0.01M AgNO_3 (d) 0.20 g nanocellulose, 0.018M trisodium citrate, 0.01M AgNO_3 .

The XRD pattern of the AgNPs showed characteristic peaks at $2\theta=29.5^\circ$, 32° , 36° , 47° (Amargeetha et al., 2018). The new peaks at $2\theta=17^\circ$, 26° , 28° and 43.5° showed the successful synthesis of stable AgNPs (Amargeetha et al., 2018). As the amount of nanocellulose stabilizing agent in the system increases, the peaks tend to shift upward and new peaks at $2\theta=50^\circ$ and 52° indicating the new crystalline states of the Ag-Cellulose intermediates formed. Distinct Bragg reflections corresponding to lattice planes (100), (010), (111), (200) and (220) at 2θ of 17° , 26° , 32° , 43.5° and 51° have been confirmed on the XRD patternsto confirm the successful synthesis of crystalline silver nano-rods, as seen in figure 7.

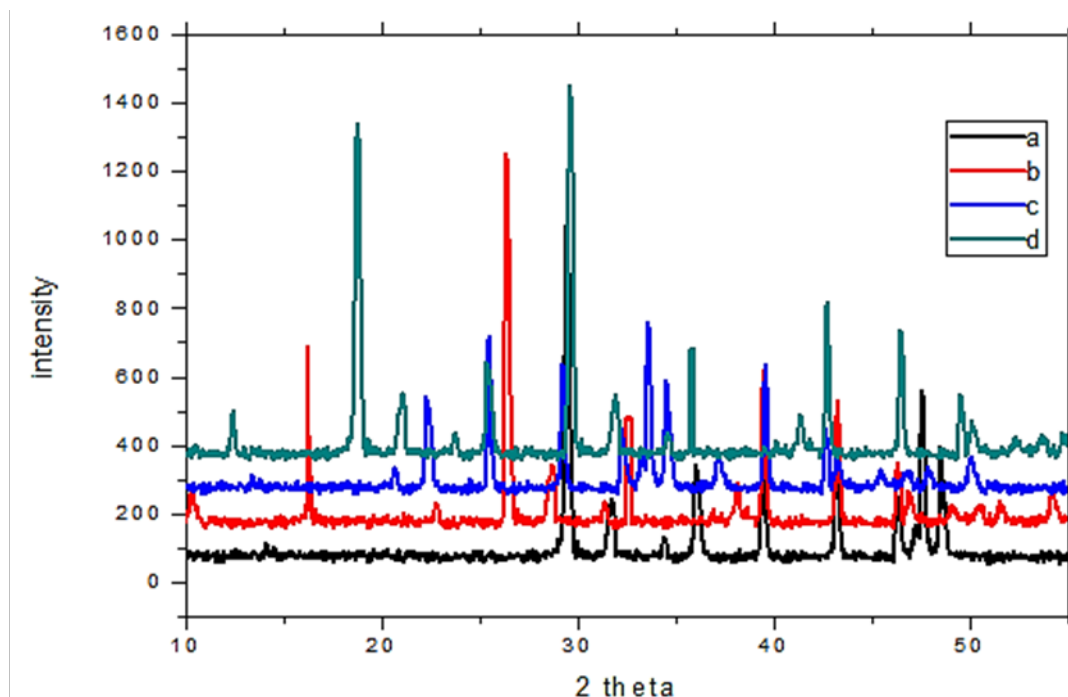


Figure 7: XRD of AgNPs synthesized using (a) 0.00g nanocellulose, 0.018M trisodium citrate, 0.01M AgNO_3 (b) 0.05g nanocellulose, 0.018M trisodium citrate, 0.01M AgNO_3 (c) 0.10g nanocellulose, 0.018M trisodium citrate, 0.01M AgNO_3 (d) 0.20g nanocellulose, 0.018M trisodium citrate, 0.01M AgNO_3 .

4.0 Conclusions

Generally, AgNPs with better performances are usually less toxic when synthesized with very low concentration of the metal precursors and reducing agents. The outcome of this research work shows that stable AgNPs can be synthesized using trisodium citrate at trace concentrations in the presence of nanocellulose as a stabilizing agent. The AgNPs synthesized with nanocellulose in this work had better optical properties than the ones synthesized without it and seems to be less aggregated in the solution after synthesis.

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