Growth Kinetic Study of Tannic Acid Mediated Monodispersed Silver Nanoparticles Synthesized by Chemical Reduction Method and Its Characterization

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ABSTRACT: The complex process of nanoparticle formation in an aqueous solution is governed by kinetics and thermodynamic factors. This paper describes a room-temperature growth kinetic study and evaluation of thermodynamic activation parameters of monodispersed silver nanoparticles (AgNPs) synthesized in alkaline medium by chemical reduction method using AgNO₃ as a source of Ag⁺ ions and tannic acid (TA) as a reductant (reducing agent) as well as a capping or stabilizing agent in the absence of any other external stabilizer. A simple and conveniently handled reaction process was monitored spectrophotometrically to study the growth kinetics in an aqueous solution as a function of the concentration of silver ion, hydroxide ion, and TA, respectively. The neutral nucleophilic group donates the electron density via a lone pair of electrons to Ag⁺ ions for the reduction process, i.e., for the nucleation of AgNPs colloid. Also, a few silver ions form a silver oxide, which also facilitates the nucleation center to enhance the growth of AgNPs colloid. The decrease and increase in rate constant on varying the TA concentration showed its adsorption onto the surface of metallic AgNPs and stabilized by polygalloyl units of TA and were the main elements to control the growth kinetics. Consequently, stabilized TA-mediated AgNPs are formed using the electron donated by quinone form of TA followed by a pseudo-first-order reaction. Apart from this, nanoparticles formed were characterized using UV-visible spectrophotometry, Fourier transform infrared spectroscopy, field emission scanning electron microscopy, energy-dispersive X-ray spectroscopy, transmission electron microscopy, and powder X-ray diffraction techniques to confirm its formation during the present kinetic study.

1. INTRODUCTION

A variety of nanomaterials of noble metals are fabricated and characterized by different routes of synthesis. Nowadays, nanoparticles of noble metals, particularly silver and gold nanoparticles, cumulate more popularity in the area of nanomaterials research because of their large surface area-to-volume ratio, which makes the diffusion process faster, their feasibility at a lower temperature, and unique physicochemical properties such as electrical, thermal, and optical properties. For the preparation of silver and gold nanoparticles, their salts are required. Comparatively, silver salts are less expensive than gold salt, so preferentially, large-scale synthesis can easily be made possible with a silver salt. Silver nanoparticles (AgNPs) possess strong surface plasmon resonance (SPR) in the visible region of an electromagnetic spectrum. These advanced nanoparticles of silver have a variety of applications in the field of electronics, imaging, biosensing, pharmaceuticals, drug delivery, catalysis, and so on. AgNPs possess strong activity against all types of microorganisms and show the highest antimicrobial activity among all noble-metal nanoparticles. Researchers have used numerous routes to prepare these nanomaterials, viz., sol-gel method, solvothermal method, microemulsion, reverse microemulsion, green synthesis, electrochemical method, laser ablation, and chemical reduction with or without capping or stabilizing agent. Depending upon the experimental conditions, method of preparation, adsorption or absorption process involved in stabilization and interaction of metal ions with a reducing agent, and concentration of each component present in the reaction, characteristics like size distribution in nanoscale range, morphology (spherical, rodlike, sheet, prismatic, triangular, etc.), stability, and physical and chemical
properties of the synthesized nanoparticles may vary strongly.\textsuperscript{35} Besides all routes, the chemical reduction method is the most famous and largely employed route for the synthesis of AgNPs due to its simplicity, high yield, and also easy handling of apparatus. In the present work, we had chosen the chemical reduction method to synthesize the AgNPs in which tannic acid (TA) behaves like a reductant (reducing agent) and capping (stabilizing) agent. A variety of reducing agents are used for the synthesis of AgNPs, but here we have chosen TA preferentially because it is a plant-based extract that is environmentally friendly, \textsuperscript{29} cost-effective for large-scale synthesis, and also reduces the addition of extra chemicals during synthesis, due to its good capping tendency. Additionally, one benefit of using TA is its high toxicological performance. The structure of TA is shown in Figure 1a,b, which has molecular formula $C_{76}H_{52}O_{46}$ with a molecular weight of 1701.2 g/mol. The antioxidant capacity, anticarcinogenic activity, and antimutagenic properties of TA are well known.\textsuperscript{35–38} It was also observed that the antioxidant and antimicrobial activities increased in thermally processed TA instead of fresh TA. It is a polyphenolic compound that chemically contains glucose moiety as the central core, and the five hydroxyl groups of the glucose are attached to the polygalloyl unit via ester bonds. Because of ester bonds, a free carboxylic acid group was not present. TA functions as a pentadentate chelating agent and capable of coordinating with 20 silver ions.\textsuperscript{39} The natural pH of the tannic acid is less than 7, and at this pH range, it behaves as a weak reducing agent.
which leads to an increase of only AgNPs at room temperature. However, nucleation of AgNPs was not possible at such a low pH.\textsuperscript{30} Glucose and gallic acid are the hydrolysis products obtained during the partial hydrolysis of TA under mild acidic or basic conditions.\textsuperscript{60} It has been reported by many researchers that gallic acid individually behaves like a good reductant (reducing agent) at alkaline pH, i.e., pH $> 7$, which successfully leads to the formation of AgNPs but was a poor stabilizer at alkaline pH, which leads to agglomeration or aggregation at room temperature. The studies also predicted that glucose individually behaves as a good stabilizer at pH $> 7$ (alkaline pH) but was a poor reductant (reducing agent).\textsuperscript{29,30,40} Therefore, it may be predicted that at alkaline pH, gallic acid behaves like a good reductant (reducing agent) and glucose behaves like a good capping or stabilizing agent at room temperature.\textsuperscript{29} Along with glucose and gallic acid, there is also the possibility of forming intermediate quinone derivative units or pyrogallol units. There are 25 phenolic hydroxyl groups in TA, out of which only 20 O-dihydroxyphenyl groups can take part in oxidation—reduction reaction, which leads to the formation of quinones and also the reduction of metal salts into metallic silver by donating electrons.\textsuperscript{40}

Although synthesis and characterization of TA-mediated AgNPs were already performed by many researchers,\textsuperscript{30,41--47} no kinetic study for the formation of AgNPs with TA by the spectrophotometric method has been yet investigated. The complex process of nanoparticle formation in aqueous solution is governed by kinetics and thermodynamic factors. However, kinetics studies of the nanoparticles are essential to know about the complex mechanistic steps involved in the reaction and to control the nanoparticle size and their size distribution in the nanoscale range. The mechanism predicts the rate-determining step involved in a particular reaction. It becomes easy to predict what factors the reaction rate depends on and how much time will be taken for a specific synthesis. With the help of kinetics, one can predict which method should be adopted preferentially for the large-scale synthesis of AgNPs at a fastest rate in lesser time.

Therefore, in the present paper, we have considered it worthwhile to perform the kinetic study of AgNPs synthesized using TA as a reductant (reducing agent) and capping agent at 30 °C. To gain better understanding, thermodynamic activation parameters for the formation of AgNPs with TA were also calculated using the Eyring equation in this work. The characterization of the TA-mediated AgNPs was done using UV–visible spectrophotometry for absorption of AgNPs with TA corresponding to a plasmon band at 410 nm.\textsuperscript{39,44,48} The characterizations were also performed using Fourier transform infrared (FTIR) spectroscopy for functional groups that surround the AgNPs surface, field emission scanning electron microscopy (FESEM) for morphological study, energy-dispersive X-ray spectroscopy (EDX) for compositional analysis, transmission electron microscopy (TEM) to know the exact morphology and average particle size, and powder X-ray diffraction (XRD) technique for determining the crystal structure as well as the average crystallite size and crystallinity index of the synthesized AgNPs.

2. SYNTHESIS OF SILVER NANOPARTICLES

The flowchart representation of a systematic procedure for the synthesis and kinetic study of silver nanoparticles is shown in Figure 2. The freshly prepared solutions were used throughout the experimental work, and all solutions were thermally equilibrated at 30 ± 0.1 °C for 30 min in a thermostat. The reaction was carried out in a glass-stoppered three-neck flask with which a condenser was connected to avoid any possible evaporation of the sample. The AgNPs were prepared by injecting the mixture of a thermally preequilibrated solution of TA whose pH was maintained at 8.5 using potassium carbonate and NaOH (to maintain the alkaline pH of the reaction mixture) in the required ratio of their concentration into the three-neck flask in which the silver nitrate solution of a required concentration was already preequilibrated at the same temperature. The formation of AgNPs was confirmed by a change in color of the solution from colorless to the formation of yellowish-brown color as shown in Figure 3a, which has a strong plasmon band at 410 nm shown in Figure 3b, and it is in confirmation with the observation of many researchers.\textsuperscript{30,44,48}

3. RESULTS AND DISCUSSION

Prior investigations showed that no AgNPs colloid formed when the reaction was performed in the absence of NaOH. Consequently, the presence of NaOH is mandatory for the synthesis of AgNPs in the solution. Our main aim is to find out the best-optimized concentrations for every individual species involved in the reaction. Therefore, we have first investigated the offset of the concentration of each reacting species involved during the course of kinetic study of the reaction. To understand the effect of each species, the kinetic study is performed for the same reaction under different sets of
concentrations of silver nitrate ranging from 0.2 to 0.6 mM, TA concentration ranging from 0.4 to 1.2 μM, and sodium hydroxide concentration ranging from 0.1 to 0.5 mM. The progress of the reaction is monitored spectrophotometrically by observing the increase in absorbance of the reaction mixture as a function of time at 410 nm (SPR band). It is essential to mention here that the increase in the absorbance of the reaction was followed till 40 min only because after that the absorbance of AgNPs colloid became invariant. Now, having observed the increase in the absorbance of AgNPs colloid formation as a function of time, the plot of ln(A∞ − As) versus time exhibited a straight line. The best result of rate constant (kobs) is assessed by the least-squares fitting method using origin software OriginPro 2018. The plot of ln(A∞ − As) versus time exhibited the highest value of regression coefficient (adj. R²) obtained using eq 1.

\[
\ln(A_\infty - A_t) = -k_{\text{obs}} \cdot t + \ln(A_\infty - A_0)
\]  

(1)

In eq 1, \(A_\infty\), \(A_t\), and \(A_0\) are the absorbances at \(t = 0\) min, absorbance at any time \(t\), and the absorbance at infinite time, respectively, of the AgNPs colloid. The values of the observed rate constants (kobs) are obtained from the slope of the ln(A∞ − As) versus time plots under different reaction sets of conditions and compiled in Table 1. For the characterization of AgNPs colloid, a typical experiment is performed at 30 °C by taking [AgNO₃] = 0.2 mM, [TA] = 0.4 μM, and [NaOH] = 0.2 mM in a 100 mL graduated flask, and finally, the required amount of DD water was added into the graduated flask, which resulted in the formation of yellow coloration, leading to the formation of AgNPs colloid. Slowly the color intensified, and finally, the color of the AgNPs colloid became dark brown, as shown in Figure 3a.

### Table 1. Study of Dependency of [AgNO₃], [NaOH], and [TA]

| [AgNO₃] (mM) | [NaOH] (mM) | [TA] (μM) | pH of sample | \(k_{\text{obs}}\) (x 10⁵ min⁻¹) | adj. R² |
|-------------|-------------|-----------|--------------|-----------------|--------|
| 0.2         | 0.6         | 0.4       | 9.66         | 7.72            | 0.987  |
| 0.3         | 0.6         | 0.4       | 9.23         | 6.69            | 0.963  |
| 0.4         | 0.6         | 0.4       | 9.17         | 6.15            | 0.970  |
| 0.5         | 0.6         | 0.4       | 9.14         | 10.64           | 0.949  |
| 0.6         | 0.6         | 0.4       | 8.87         | 9.2             | 0.963  |
| 0.2         | 0.1         | 0.8       | 8.57         | 13.67           | 0.959  |
| 0.2         | 0.2         | 0.8       | 8.61         | 9.97            | 0.989  |
| 0.2         | 0.3         | 0.8       | 8.71         | 3.86            | 0.970  |
| 0.2         | 0.4         | 0.8       | 8.79         | 4.17            | 0.988  |
| 0.2         | 0.5         | 0.8       | 8.99         | 6.60            | 0.987  |
| 0.2         | 0.6         | 0.8       | 9.66         | 4.31            | 0.994  |
| 0.2         | 0.6         | 0.4       | 9.66         | 7.72            | 0.987  |
| 0.2         | 0.6         | 0.6       | 9.57         | 6.98            | 0.943  |
| 0.2         | 0.6         | 0.8       | 9.42         | 4.31            | 0.979  |
| 0.2         | 0.1         | 1.0       | 9.40         | 2.19            | 0.980  |
| 0.2         | 0.6         | 1.2       | 10.41        | 19.3            | 0.966  |

3.1. Characterization of Synthesized Silver Nanoparticles. For the confirmatory analysis, gray-colored AgNPs powder is obtained after centrifuging the stock solution of AgNPs colloid at 3000 rpm for 45 min. The powdered sample is obtained (after decantation of supernatant liquid) and washed several times with DD water to remove the impurities from the surface of AgNPs and then dried thoroughly and stored in an airtight container for further use.

3.1.1. FTIR Analysis of Prepared Silver Nanoparticles. FTIR analysis is performed to gain information about the functional group adsorbed on the surface of AgNPs and is given in Figure 4. Since it is already mentioned that TA is a plant-based extract, depending upon the origin of TA, the band intensity and/or position in the spectra may be quite different from the spectra given by other investigators. A band centered at 3590 cm⁻¹ is due to stretching of −OH groups. A broad band that appeared at 3165 cm⁻¹ is due to the aromatic sp² C−H stretching frequency. A band at 2882 cm⁻¹ is due to the C−H stretching of the aliphatic methane group. A weak band at 2178 cm⁻¹ is due to an aromatic overtone of the C−H group bending. A band at 1673 cm⁻¹ due to the C=O stretching revealed the existence of TA in quinone form during synthesis. A band at 1531 cm⁻¹ is due to the stretching of the aromatic C=C group. A band at 1396 cm⁻¹ is due to the stretching of the COO− group observed, which confirms that TA was adsorbed onto the surface of AgNPs through this group only. A band at 1049 cm⁻¹ is due to the ring stretching or in-plane bending of the C−H group. A band lower than 1000 cm⁻¹, i.e., at 985 and 687 cm⁻¹, is due to the interatomic absorption vibration of silver metal in the fingerprint region.

3.1.2. FESEM and EDX Analyses of Silver Nanoparticles. For obtaining surface morphology and nanostructural studies, FESEM analysis has been performed. FESEM images at 5 μm ((≈20,000 magnification) and 500 nm ((≈2 00 000 magnification) scales of synthesized AgNPs coated on a silicon (Si/SiO₂) substrate obtained are represented in Figure 5a,b, which indicated the quasi-spherical nature of AgNPs. The EDX analysis confirms the formation of AgNPs from silver ions because a signal is obtained in the region of silver, i.e., ≈3 keV, as shown in Figure 5c. It is essential to mention that the material was coated on a silicon substrate, so there must be a strong signal corresponding to the silicon (i.e., at ~1.5 keV) in the profile. It also revealed that the percentage weight composition of silver (61.86) is significant compared to oxygen (32.82) and carbon (5.32), which can be seen in the pie chart represented in Figure 5d. The signals of carbon and oxygen are also present in the profile because synthesized AgNPs are stabilized by TA, which contains carbon and oxygen atoms. A prominent peak of oxygen is may be due to adsorption of TA through the oxygen center onto the surface AgNPs. Hence, this confirms the complete reduction of silver into AgNPs.
3.1.3. TEM Study of Silver Nanoparticles.

To know the exact morphology of the synthesized AgNPs more clearly, TEM analysis is performed. Prior to analysis, a carbon-coated copper grid is prepared by aliquots of approximately dilute sample, which is sonicated for 2 min, and then the grid is allowed to dry under ambient conditions. The recorded TEM

Figure 5. FESEM images of silver nanoparticles (a) 5 μm and (b) 500 nm. (c) EDX profile of silver nanoparticles. (d) Pie chart of percentage weight composition of elements detected in the EDX profile of silver nanoparticles.

Figure 6. TEM images of silver nanoparticles: (a) 50 nm and (b) 20 nm. (c) Histogram analysis of TEM of silver nanoparticles.
images at 50 and 20 nm scales of the AgNPs are represented in Figure 6a,b. A histogram is plotted, as shown in Figure 6c, by analysis of 36 particles using ImageJ software to calculate the average particle size of the synthesized AgNPs. The spherical shape of the AgNPs observed by TEM analysis shows good resemblance with the morphology depicted by FESEM study (vide supra, Section 3.1.2) and hence confirmed the spherical shape of the synthesized nanoparticles with the size distribution between 5 and 40 nm having an average particle diameter of 18.20 nm with a standard deviation (σ) of 0.302 nm, indicating narrow size distribution of particles.

3.1.4. XRD Study of Silver Nanoparticles. XRD analysis is performed to confirm the crystalline nature of synthesized AgNPs. The diffraction pattern of AgNPs is presented in Figure 7a. The diffraction peak at 2θ = 37.98, 44.16, 64.36, and 77.34°, corresponding to (111), (200), (220), and (311) planes, are observed and showed good resemblance with JCPDS card no. 04-0783, which attributes the cubic structure of AgNPs. Also, it has been observed by many investigators that the most intense peak for the (111) plane is generally shown by the face-centered cubic structure. Therefore, it may be predicted that the synthesized particles have a face-centered cubic (FCC) structure having the orientation of crystal growth along the (111) plane. The theoretical parameters obtained with the help of XRD data are provided in Table 2. The value of d-spacing is calculated using Bragg’s law represented by eq 2. The average crystallite size of AgNPs is 22.987 nm, which is calculated using the Debye–Scherrer formula represented by eq 3, where D, λ, β, and θ are the average crystallite size, wavelength of source used, full width at half-maximum (FWHM) of the peak (in radians), and Bragg’s angle, respectively. Moreover, the mean of the lattice parameter “a” of the AgNPs is 4.075 Å, which is calculated using eqs 2 and 4.

### Table 2. List of Theoretical Parameters Obtained from XRD Data

| 2θ (deg) | d-spacing (in nm) | average crystallite size (D) (in nm) | lattice parameter (a) (in Å) |
|----------|-------------------|------------------------------------|-----------------------------|
| 37.98    | 0.0066            | 0.236                              | 22.210                      | 4.08            |
| 44.16    | 0.0067            | 0.204                              | 23.325                      | 4.08            |
| 64.36    | 0.0070            | 0.144                              | 23.395                      | 4.07            |
| 77.34    | 0.0074            | 0.123                              | 24.020                      | 4.07            |

2d sin θ = nλ

\[ D = \frac{0.9\lambda}{\beta \cos \theta} \]

\[ d_{\text{lat}} = \frac{a}{\sqrt{(h^2 + k^2 + l^2)}} \]

\[ \beta \times \cos \theta = k\lambda/D + 4e \sin \theta \]

\[ \delta = 1/D^2 \]

It is important to mention here that the broadness in the diffraction peak is due to the very small crystallite size and strain. The broadening in the diffraction peak of the sample is described by eq 5, where β, θ, D, λ, and ε are full width at half-maxima of the peak, diffraction angle, average crystallite size, wavelength of X-ray, and strain, respectively. For calculating the accurate average crystallite size, the Williamson–Hall plot of AgNPs, represented by Figure 7b, is drawn by plotting β cos θ on the y-axis and 4 sin θ on the x-axis, a straight line with regression coefficient value 0.99 is obtained with slope equal to 4ε and intercept equal to kλ/D. The strain and the average crystallite size of AgNPs calculated using the W–H plot are found to be 2.286 × 10⁻⁵ and 22.28 nm, respectively. The negative slope value suggested that the synthesized AgNPs are compressive. The hardness of the material can also be explained in terms of dislocation density, i.e., the smaller the crystallite size, the more prominent is the dislocation density, and hence the harder the material. The line dislocation density (δ) of the synthesized AgNPs is calculated using eq 6 and is found to be 20.145 × 10⁻¹⁴ m⁻².

The absorption spectra of the prepared AgNP colloid at different wavelengths are recorded as shown in Figure 3b by a blue line. It has been observed that one sharp peak at 410 nm appeared corresponding to the maximum absorbance, due to the SPR band of colloidal silver. However, the black line in the spectra given in Figure 3b for TA exhibited two bands corresponding to π–π* and n–π* energy transitions, while no peak at 410 nm appeared in the absorption spectra of TA solution, and hence it...
confirmed the formation of AgNPs colloid. The inset graph in Figure 3b shows the repetitive spectral scan for the reaction under the reaction condition [AgNO3] = 0.2 mM, [NaOH] = 0.6 mM, and [TA] = 0.4 μM, which suggested that the wavelength at 410 nm increases with time and it does change during the course of a reaction. The color of the AgNPs colloid and λ\text{max} shows a good resemblance with previous observations of various investigators.7,54 The absorption spectra and the color of the prepared AgNPs colloid are found to be highly dependent upon the method of synthesis, nature of reductant, nature of surfactant, acidity or basicity of the reaction mixture, and the presence or absence of stabilizing or capping agent.

3.3. Optimization of Different Variables for Kinetic Study. 3.3.1. Dependency of Reaction rate on [AgNO3]. The dependency of [AgNO3] on the rate of formation of AgNPs colloid is studied at 0.2 ≤ [AgNO3] ≥ 0.6 mM with 0.6 mM NaOH and 0.4 μM TA. The spectra of the evolution of absorbance at wavelength 410 nm versus time for all experiments for the variation of [AgNO3] result in exponential growth for the formation of AgNPs colloid and shown in Figure 8a. The rate constant (k_{obs}) of the formation of AgNPs colloid is calculated from the slope of the plot of ln(A∞ − A_t) versus time represented by Figure 8b. At a lower concentration of silver ions, i.e., [AgNO3] = 0.1 mM, the transformation of silver ions into AgNPs colloid is not observed, and hence the kinetic study at such a low concentration is not possible. At 0.5 ≤ [AgNO3] ≥ 0.3 mM, the color of AgNPs colloid turns yellowish-brown and the velocity constants (k_{obs}) are found to be 7.72 × 10^{-3}, 6.69 × 10^{-3}, 6.15 × 10^{-3}, and 10.64 × 10^{-3} min\(^{-1}\) and for silver-ion concentrations 0.2, 0.3, 0.4, and 0.5 mM with regression coefficients (adj. R\(^2\)) of 0.987, 0.963, 0.970, and 0.949 respectively. At a higher concentration of silver ions, i.e., [AgNO3] ≥ 0.6 mM, k_{obs} are 9.2 × 10^{-3} min\(^{-1}\) with adj R\(^2\) value 0.963, and this value remains unchanged with silver-ion concentration ranging between 1.2 ≤ [AgNO3] ≥ 0.6 mM and shows that the rate of formation of AgNPs colloid with respect to silver-ion concentration is of zero order. At a higher concentration of silver ions, the kinetic study is hampered and attributed to the agglomeration of silver colloid, which occurred due to the precipitation of large gray-colored silver particles.7 This decrease in the k_{obs} value can be justified by considering the role of hydroxide ion present in the reaction mixture. Only a sufficient number of silver ions are there to react with hydroxide ions at lower concentrations, and hence AgNPs colloid is formed from all of the silver ions.55 But as the concentration of silver ions increased, the number of silver ions present in the reaction mixture is increased, a few of which under alkaline condition produce Ag2O, which will enhance the formation of silver colloid because the Ag2O surface will facilitate the nucleation center to enhance the transformation, i.e., the growth of AgNPs colloid formed on oxide surface becomes constant, and consequently a decrease in the value of rate constant was observed. The formation of silver oxide is also supported by XRD studies (vide supra, Section 3.1.3) as there is a diffraction peak at plane (111), which evident as silver exists in the form of silver oxide.

![Figure 8](https://doi.org/10.1021/acsomega.1c03100)

**Figure 8.** (a) Evolution of absorbance at 410 nm of silver nanoparticle colloid formation at 0.6 mM NaOH, 0.6 μM TA, and different [AgNO3]. (b) Plot of ln(A∞ − A_t) versus time at 0.6 mM NaOH, 0.6 mM TA, and different [AgNO3].

![Figure 9](https://doi.org/10.1021/acsomega.1c03100)

**Figure 9.** (a) Evolution of the absorbance at 410 nm of silver nanoparticle colloid formation at 0.2 mM AgNO3, 0.8 μM TA, and different [NaOH]. (b) Plot of ln(A∞ − A_t) versus time at 0.2 mM AgNO3, 0.8 μM TA, and different [NaOH].
3.3.2. Dependency of Reaction Rate on [NaOH]. The dependency of [NaOH] on the rate of formation of AgNPs colloid is studied at 0.1 ≤ [NaOH] ≥ 0.6 mM with 0.2 mM AgNO₃ and 0.8 μM TA. The spectra of the evolution of absorbance at wavelength 410 nm versus time for all experiments for the variation of [NaOH] resulted in exponential growth in the formation of AgNPs colloid and are shown in Figure 9a. It is important to mention here that no Figure 10. (a) Evolution of the absorbance at 410 nm of AgNP colloid formation at 0.2 mM AgNO₃, 0.6 mM NaOH, and different [TA]. (b) Plot of ln(A∞ − At) versus time at 0.2 mM AgNO₃, 0.6 mM NaOH, and different [TA].

Scheme 1. Plausible Mechanism for the Formation of Silver Nanoparticle Colloid

Scheme 1
AgNPs colloid is formed in the absence of NaOH. The rate constant \((k_{obs})\) of formation of AgNPs colloid is calculated from the slope of the plot of \(\ln(A_0 - A_t)\) versus time and is represented in Figure 9b. At \(0.3 \leq [\text{AgNO}_3] \leq 0.1 \text{ mM}\), the velocity constants \((k_{obs})\) are \(13.67 \times 10^{-3}\), \(9.97 \times 10^{-3}\), and \(3.86 \times 10^{-3} \text{ min}^{-1}\) for hydroxide-ion concentrations 0.1, 0.2, and 0.3 mM, with regression coefficient values (adj. \(R^2\)) of 0.959, 0.989, and 0.970 respectively. Above this concentration of hydroxide ions, the rate constant is \(4.31 \times 10^{-3} \text{ min}^{-1}\) having a regression coefficient value (adj. \(R^2\)) equal to 0.994, and this value remains unchanged with further increase in the concentration of hydroxide ions, which shows that the rate of formation of AgNPs colloid is independent with respect to hydroxide-ion concentration. The observed decrease and increase in the behavior of rate constant might be due to the conversion of phenolic form to quinone form of TA as shown in eq 7. Furthermore, it is predicted that the rate constant is very sensitive even at a lower concentration of hydroxide ions, i.e., a small amount of \([\text{NaOH}]\) was enough for the nucleation of AgNPs colloid from silver ions.

3.3.3. Dependency of the Reaction Rate on Reducing Agent, [TA]. The dependency of [TA] on the rate of formation of AgNPs colloid is studied between 1.2 \(\mu\text{M} \leq [\text{TA}] \geq 0.4 \mu\text{M}\) with 0.2 mM AgNO\(_3\) and 0.6 mM NaOH. The spectra of the evolution of absorbance at wavelength 410 nm versus time for all experiments for the variation of [TA] resulted in exponential growth in the formation of AgNPs colloid and are shown in Figure 10a. The rate constant \((k_{obs})\) of the formation of AgNPs colloid is calculated from the slope of the plot of \(\ln(A_0 - A_t)\) versus time, as represented in Figure 10b. At the concentration range 1.0 \(\mu\text{M} \leq [\text{TA}] \geq 0.4 \mu\text{M}, the rate constants are \(7.72 \times 10^{-3}, 6.98 \times 10^{-3}, 4.31 \times 10^{-3},\) and \(2.19 \times 10^{-3} \text{ min}^{-1}\), respectively, with regression coefficient (adj. \(R^2\)) values 0.987, 0.943, 0.979, and 0.980, respectively. At [TA] = 1.2 \(\mu\text{M}\), the rate constant was \(19.3 \times 10^{-3} \text{ min}^{-1}\) with regression coefficient value 0.966. On further increase in [TA], instantly, there is a formation of dark brown AgNPs colloid due to which kinetic study become complicated at a higher concentration of TA. The decrease and increased in the behavior of the rate constant during the formation of AgNPs colloid may be attributed to the adsorption of TA onto the surface of metallic AgNPs. The SPR band of the AgNPs is stable due to which kinetic study become complicated at a higher concentration of TA. Hence, it may be predicted that the AgNPs colloid formed during the experiment is self-stabilized, and it does not need any external stabilizer.

Using the above predictions and observations, Scheme 1 has been proposed for the formation of AgNPs colloid from silver ions using TA as a reducing agent. The step, represented by the equilibrium condition in Scheme 1, showed the conversion of phenolic form TA to quinone form of TA in hydroxide ions. The nucleation of AgNPs colloid via conversion of Ag(1) into Ag(0) using the electron donated by the quinone form of TA is given by eq 8.60 It is important to mention here that only a few of the silver ions are involved in the nucleation. However, a few of them were converted into Ag\(_2\)O because silver ions show the existence in the form of oxide in an alkaline medium responsible for the formation of AgNPs colloid.7,58 Since no turbidity is observed in the reaction mixture, it is assumed that the silver oxide species must be there in the colloid form and it is also supported by XRD study (vide supra, Section 3.1.3). The adsorption of the silver ions onto the silver oxide surface is given by eq 9. Then, the resulting species accept an electron from the \(-\text{OH}\) group of TA (quinone form), leading to the formation of radical of TA and an electron-rich Ag\(_2\)O-(Ag\(^+\)) species, represented by eq 10. Since the electron transfer involved in this step is slow, it is the rate-determining step for this reaction. The fast electron transfer from radical to Ag\(_2\)O-(Ag\(^+\)), species leads to the formation of Ag\(_2\)O-(Ag\(^+\)) species, and oxidized TA is shown in eq 11. The conversion of Ag\(_2\)O-(Ag\(^+\)) to e\(^-\)(Ag\(_2\)O), as shown in eq 12, which further reacts with silver ions to form Ag(0), is represented in eq 13. Both eqs 14 and 15 represent the growth of AgNPs colloid, and the adsorption of TA onto silver ions is represented in eq 16, which is also supported by the EDX profile in Figure 5d as it possesses signals of carbon and oxygen atoms (vide supra, Section 3.1.2).

3.4. Thermodynamic Activation Parameters. The thermodynamic activation parameters, i.e., change in enthalpy of activation (\(\Delta H^\ddagger\)) and change in entropy of activation (\(\Delta S^\ddagger\)) of the reaction, are evaluated using Eyring eq 17 by performing the same reaction at three different temperatures. The other parameters such as a change in Gibbs’s free energy of activation (\(\Delta G^\ddagger\)), the activation energy (\(E^\ddagger\)), and equilibrium constant for the activated state (\(K^\ddagger\)) are calculated using other thermodynamic eqs 18–20, respectively.

\[
\ln \left( \frac{k_{obs} h}{k_B T} \right) = \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT} \tag{17}
\]

\[
\Delta G^\ddagger = \Delta H^\ddagger - T \Delta S^\ddagger \tag{18}
\]

\[
E^\ddagger = \Delta H^\ddagger + RT \tag{19}
\]

\[
\Delta G^\ddagger = -RT \ln K^\ddagger \tag{20}
\]
activation parameters, reaction mixtures are prepared by adding 0.2 mM AgNO₃, 0.2 mM NaOH, and 0.4 μM TA in the appropriate ratio of their volumes, and a kinetic study is made at three different temperatures viz. 30, 40, and 50 °C respectively. The rate constant for the formation of AgNPs is calculated at each temperature from the slope of the plot of \( \ln(A_\infty - A_t) \) versus time, as shown in Figure 11a. The rate constants (\( k_{obs} \)) at 30, 40, and 50 °C are equal to \( 5.34 \times 10^{-3}, 8.39 \times 10^{-3}, \) and \( 10.04 \times 10^{-3} \) min⁻¹ with regression coefficients 0.99, 0.97, and 0.97, respectively. The plot of the left-hand side of eq 17 versus \( 1/T \) yields a straight line having a regression coefficient of 0.99, and is shown in Figure 11b. The values of \( \Delta S^a \) and \( \Delta H^a \) are evaluated from the intercept and slope of the plot in Figure 11b and are found to be \( -210.84 \) and 23.62 kJ mol⁻¹, respectively. At 25 °C, the values of \( \Delta G^*, E_1^*, \) and \( K^* \) for the formation of AgNPs colloid are calculated by using eqs 18–20 as 86.44 kJ mol⁻¹, 26.10 kJ mol⁻¹, and 7.04 \( \times 10^{-10} \) respectively. During the course of the reaction, a rigid activated complex as a transient intermediate is formed due to which there is a decrease in the degree of freedom of the reacting system. This decrease in degree of freedom is depicted by the negative value of change in entropy of activation, which is calculated earlier.

4. CONCLUSIONS

In the present paper, an approach for the kinetic study and thermodynamics activation parameters of TA-mediated synthesis of monodispersed AgNPs via a chemical reduction method has been given. TA is preferentially chosen for this synthesis because it is a plant-based extract, environmentally friendly, and shows good toxicological performance. It is found that on increasing the number of silver ions in the reaction mixture, a few silver ions produce silver oxide, which facilitates the nucleation center to enhance the transformation. However, at higher concentrations of silver ions, the kinetic study was hampered due to the agglomeration of AgNPs colloid. While varying the concentration of hydroxide ions, it is found that a small amount of NaOH is enough for the nucleation of AgNPs colloid. It can also be concluded from the kinetic study that the reduction of Ag⁺ takes place through the neutral nucleophilic group, which donates the electron density via a lone pair of electrons for the nucleation of AgNPs colloid. The mechanistic studies showed that the rate-determining step in the reaction involves electron transfer, and the reaction follows pseudo-first-order kinetics. Since no alteration in the absorbance of AgNPs was observed, it is evident that TA can act as an excellent reductant (reducing agent) and a good capping or stabilizing agent, which also eliminates the addition of an external stabilizing agent. However, from the study of thermodynamic activation parameters, it can be concluded that during the course of the reaction, the negative value of change in entropy of activation evidences a rigid activated complex as a transient intermediate, which results in a decrease in the degree of freedom of the reacting system. Finally, from the kinetic studies, it can be concluded that it is a simple, rapid, environmentally friendly, and economically viable method for the synthesis of monodispersed AgNPs with smaller diameters, which can be easily used in the future for pharmaceuticals, electronics, drug delivery, etc. and also an excellent approach for large-scale synthesis.

5. EXPERIMENTAL SECTION

5.1. Chemicals.

Chemicals used for synthesis, including silver nitrate (AgNO₃, 99.9%), tannic acid (TA, 98%), potassium carbonate (K₂CO₃, 99%), and sodium hydroxide (NaOH, 99%), were purchased from E. Merck Ltd., Mumbai, India. Analytical-grade chemicals were used without further purification during the entire experimental work. All of the glassware was washed with aqua regia, followed by distilled water, and dried in an oven. All of the stock solutions were prepared in double-distilled (DD) water. The stock solution of NaOH was prepared by dissolving 0.08 g of compound in 100 mL of DD water, and the required amount of DD water was added and finally made it up to the mark. The stock solution of 0.39 mM TA was prepared by dissolving 0.0680 g of silver salt in it, and the required amount of DD water was added and finally made it up to the mark. The stock solution of 0.39 mM TA was prepared by dissolving 0.0680 g of compound in 100 mL of DD water, and the pH of the solution was maintained at 8.5 using a concentrated solution of potassium carbonate. The stock solution of NaOH was prepared by dissolving 0.08 g of compound in 100 mL of DD water. A freshly prepared solution was used for each sample preparation every time in the present study.

5.2. Physical Techniques.

The pH measurements of all of the samples and the stock solutions were made on a Systronic pH meter (model 361). Recording of absorption spectra and kinetic measurements were performed using a UV–visible double-beam spectrophotometer (LAB UV Next Generation) equipped with a A-100 constant-temperature sipper system throughout the present study. A Remi thermostat was used to maintain the temperature of the reaction system throughout the reaction.
For the study of the functional group attached with synthesized material, a Fourier transform infrared (FTIR) spectrometer of Thermo Scientific Nicolet 6700 was used. To observe surface morphology and elemental composition of synthesized AgNPs, a field emission scanning electron microscope (FESEM) of JFEI, Nova Nano SEM-450, was used. Transmission electron microscopy (TEM) was done to determine the exact morphology and average particle size of the synthesized material using a Talos machine operating at 200 kV. X-ray diffraction was done to study the lattice plane, crystal structure, and the average crystallite size of the synthesized AgNPs on Rigaku, SmartLab 9 kW, rotating anode X-ray diffractometer using a Cu Kα X-ray of wavelength 1.54 Å in a 2θ range of 10°–90°.

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**NOMENCLATURE**

**Abbreviation**

AgNPs silver nanoparticles
TA tannic acid
FCC face-centered cubic
UV-Vis ultraviolet–visible
FTIR Fourier transform infrared
FESEM field emission scanning electron microscopy
EDS energy-dispersive X-ray spectroscopy
TEM transmission electron microscopy

XRD X-ray diffraction
W-H Williamson–Hall
SPR surface plasmon resonance
DD double-distilled
CTAB cetyltrimethylammonium bromide
SDS sodium dodecyl sulfate
FWHM full width at half-maxima

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