Kinetic and Mechanistic Studies of the Formation of Silver Nanoparticles by Nicotinamide as a Reducing Agent

Indresh Kumar, Chinky Gangwar, Bushra Yaseen, Pradeep Kumar Pandey, Sheo K. Mishra, and Radhey Mohan Naik*

ABSTRACT: Here, in the present study, silver nanoparticles (SNPs) in the size range 6–10 nm have been synthesized by a chemical reduction method using nicotinamide (NTA), an anti-inflammatory agent, and cetyltrimethylammonium bromide (CTAB), a good stabilizing agent, to preparing the nanoparticles in the 6–10 nm size range. Kinetic studies on the formation of SNPs have been performed spectrophotometrically at 410 nm (strong plasmon band) in aqueous medium as a function of [AgNO₃], [NTA], [NaOH], and [CTAB]. The plot of ln(A∞ − At) versus time exhibited a straight line and the pseudo-first-order rate constants of different variables were calculated from its slope. On the basis of experimental findings, a plausible mechanism was proposed for the formation of SNPs colloid. From the mechanism, it is proved that the reduction of silver ions proceeded through the formation of silver oxide in colloidal form by their reaction with hydroxide ions and NTA after performing their function and readily undergo hydrolysis to form nicotinic acid as a hydrolysis product with the release of ammonia gas. The preliminary characterization of the SNPs was carried out by using a UV-visible spectrophotometer. The detailed characterization of SNPs was also carried out using other experimental techniques such as Fourier transform infrared spectroscopy (FTIR), field-emission scanning electron microscopy (FESEM), energy-dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM), and powder X-ray diffraction (PXRD). SNPs show a remarkable catalytic activity of up to 90% for the reduction of the cationic dye methylene blue.

1. INTRODUCTION

Recently, nanostructured materials have turned into one of the most promising themes that contributes to the majority of fields, including chemistry, physics, biology, and engineering, with various breakthroughs that will enhance the application of nanomaterials. Currently, inorganic nanomaterials including zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) materials have attracted increasing attention due to their physicochemical properties being different from those of their bulk part. We have mainly focused on 0D inorganic nanomaterials, i.e., metal or metal oxide nanoparticles, because of their high surface area to volume ratio, sharp size distribution in the range of 1–100 nm, and uniformity in their shape.

Nanoparticles in the elemental form of metals, especially of Ag, Au, Fe, Cu, Pt, Pd, Ni, and Co, have been widely used for their antimicrobial, optical, catalytic, electronic, and sensing properties and also as doping agents. Nanoparticles have also been employed in different fields such as health care, cosmetics, food industries, environmental remediation, optics, biomedical sciences, chemical industries, electronics, drug delivery, energy science, optoelectronics, catalysis, etc. The two major approaches for the synthesis of nanoparticles are the bottom-up and top-down approaches.

In addition, the fabrication of discrete nanomaterials with a size of between 1 to 20 nm is noteworthy because of their high diffusion rate, which results in an enhanced tendency of adsorption and makes them more beneficial in environmental remediation and drug delivery. Therefore, in the present study, we have targeted to synthesizing silver nanoparticles (SNPs), as they are well-known for their biological importance and are cheaper than other noble-metal salts.

To emphasize, with the growing concern regarding the environmental and biological effects of nanoparticles, it is

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crucial to find an eco-friendly method for the formation of nontoxic “green” nanoparticles without incorporation of toxic chemicals, hazardous solvents, etc. Encouragingly, several investigators have provide an approach toward the environmentally benign synthesis of metallic nanoparticles by using amino acids and drugs such as isoniazid, paracetamol, vitamin C, trypsin, gabapentin, dopamine, etc. Accordingly, we have tried to establish a method for the formation of SNPs by using nicotinamide (NTA) as a reducing agent. Figure 1 shows the structural formula of NTA, which is also known as niacinamide. It is widely used as a medicine. The determination of NTA and studies on its hydrolysis product via spectrophotometric methods have received the attention of several investigators. The huge interest in the use of NTA as a reducing agent is due to its high solubility in water, greater extent of stability (i.e., a 10% solution of NTA in water may be autoclaved without any degradation at 120 °C for 20 min), and its layer-forming property over nanoparticles surface.

Therefore, we have considered it worthwhile to investigate the formation of SNPs colloid through a growth kinetic study by adopting a chemical reduction method in which NTA has been used as a reducing agent and checking the effect of an external stabilizer on the kinetic study at 25 ± 0.1 °C. The kinetic study of nanoparticle formation was carried out spectrophotometrically at 410 nm (strong plasmonic band) by monitoring the increase in absorbance as a function of time under different experimental conditions. A kinetic study on nanoparticles formation can be a good tool to predict the most plausible mechanism through which the formation of SNPs takes place and yields the desired product. The preliminary characterization of SNPs prepared by using NTA as a reducing agent was carried out with a UV−visible spectrophotometer by recording the absorption spectra of SNPs. Other experimental techniques employed for the characterization of SNPs were Fourier transform infrared spectroscopy (FTIR), field-emission scanning electron microscopy (FESEM), energy-dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM), and powder X-ray diffraction (PXRD). Furthermore, the applicability of the prepared SNPs was tested for the catalytic reduction of the cationic dye methylene blue for the treatment of wastewater coming from textile industries.

2. EXPERIMENTAL SECTION

2.1. Chemicals. Materials used for the preparation of SNPs colloid were silver nitrate (10−2 M AgNO3) from E. Merck Ltd., Mumbai, India, sodium hydroxide (2 × 10−2 M NaOH) of analytical grade form SD Fine-Chem Ltd., cetyltrimethy lammonium bromide (10−2 M CTAB) from the BDH laboratory chemicals division, and nicotinamide (10−2 M NTA) from E. Merck Ltd., Mumbai, India, as a reducing agent. Methylene blue (10−3 M MB in ethanol) was purchased from...
Hi Media Laboratories Pvt. Ltd., Bombay, India. All chemicals were used without further purification.

2.2. Instrumentation. For kinetic measurement and absorption spectra, a LAB UV Next Gen UV–visible double beam spectrophotometer equipped with an A-100 constant-temperature sipper system was used. A Thermo Scientific Nicolet 6700 Fourier transform infrared (FTIR) spectrometer was used for the study of the functional group linked with the prepared SNPs. A JFEI, Nova Nano SEM-450 field-emission scanning electron microscope (FESEM) was used to observe the surface morphology of the prepared SNPs. Transmission electron microscopy (TEM) on a Talos machine operating at 200 kV was used to gain information about the exact morphology and average particle size of the prepared SNPs. X-ray diffraction on a Rigaku SmartLab 9 kW rotating-anode X-ray diffractometer using Cu Kα X-radiation with λ = 1.54 Å was used to study the lattice plane, crystal structure, and particle size of the prepared SNPs.

2.3. Synthesis and Kinetics of Silver Nanoparticles. Freshly prepared thermally equilibrated solutions at 25 ± 0.1 °C for 1/2 h in a thermostat were used throughout the present study. A glass-stoppered two-necked flask was used to carry out the reaction, which was fitted with a condenser to eliminate the chances of evaporation. The SNPs colloid was obtained by the reduction of AgNO₃ by injecting NTA in the presence of already pre-equilibrated CTAB (as a stabilizer) and NaOH solution (to maintain the alkaline pH) at 25 ± 0.1 °C in the required amount into the two-necked flask.

3. RESULTS AND DISCUSSION

Preliminary observations suggested that the formation of SNPs by the reduction of silver nitrate by using NTA at room temperature does not take place in the absence of hydroxide ions. The formation of SNPs was confirmed by a change in color of the solution from colorless to pink, as shown in Figure 2a, and the solution has a strong plasmon band at 410 nm, as shown in Figure 2b, in agreement with similar observations by other researchers. However, it is pertinent to acknowledge that the absorption spectrum of pure NTA contains two peaks at 300 and 260 nm, as shown in Figure 2c, which can be easily used to differentiate them from the peak observed in Figure 2b. Here, in the present experiment, to study the effect of external stabilizers, a cationic surfactant, i.e., CTAB, and an anionic surfactant, SDS were used. Several trials were performed to select the best stabilizer for the formation of SNPs, which indicated that CTAB is suitable for SNPs formation. However, SDS created a disturbance in the system by a loss of transparency and it became rather difficult for the spectrophotometer to give correct values of absorbance. Hence, in all of the further processes, CTAB was used as one of the parameters throughout the experimental work.

During the initial time between 0 and 20 min, only a slight change in the absorbance was observed. Between 20 and 40 min, a broad absorption peak centered at 410 nm was developed. Later, at various reaction times, a continuous increase in the intensity of an absorbance leading to the formation of a sharp or intense peak at 410 nm was noticed, which confirms the formation of SNPs colloidal, as shown in Figure 2d. It is important to acknowledge that no significant changes were observed in the absorption spectra upon aging the SNPs colloidal in the dark for several days or weeks; only a very slight change, i.e., an increase in a maximum absorbance value corresponding to λmax was observed for the same colloidal solution. The change in intensity of the SNPs colloidal solution could be seen by the naked eye via a change from pink to pinkish red, also shown in Figure 3a. To study the growth kinetics of the reaction of SNPs formation, different sets of the reaction mixture were prepared by varying [AgNO₃], [NaOH], [NTA], and [CTAB]. To get the most appropriate result of rate constant (kobs), a least-squares fitting technique was adopted to observe the effect of each parameter. The highest value of the regression coefficient, i.e., adjusted R² was observed for eq 1 on plotting the graph between ln(Ano − Ao) and time.

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

In eq 1, \( A_0 \) is the absorbance at \( t = 0 \) min, \( A_t \) is the absorbance at any time \( t \), and \( A_{\infty} \) the absorbance at infinite time of the SNPs colloidal. The data collected for the rate constants (kobs) corresponding to the variation of all the experimental variables are given in Table 1. Prior to studying the kinetics, a confirmation of the formation of SNPs was mandatory. Therefore, the identification or characterization of the SNPs was made by employing several techniques: viz., UV–visible spectrophotometry (UV–vis), Fourier transform infrared spectroscopy (FTIR), field emission scanning electron microscopy (FESEM), energy-dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM), and powder X-ray diffraction (PXRD).

3.1. Characterization. Preliminary characterization of each set of samples was carried out with a UV–vis spectrophotometer, and the formation of SNPs were confirmed by obtaining an absorption maximum, i.e. 410 nm, that lies in the surface plasmonic resonance range of SNPs. However, another characterization has been carried out for powdered SNPs obtained by centrifugation (3000 rpm for 30 min) of the stock solution prepared by mixing 0.2 × 10⁻³ M AgNO₃, 0.2 × 10⁻³ M NaOH, 0.2 × 10⁻³ M CTAB, and 0.2 × 10⁻³ M NTA under the same experimental conditions.

3.1.1. FTIR Analysis. The study of functional groups attached to the outer surface of SNPs was analyzed with the help of FTIR spectra recorded between 3800 and 500 cm⁻¹, as shown in Figure 3. A sharp band at 3393 cm⁻¹ appears due to N–H and O–H stretching. A band at 1654 cm⁻¹ appears due
to >C≡N stretching. A band at 1393 cm$^{-1}$ appears due to C≡N stretching. A band at 1140 cm$^{-1}$ appears due to C−O stretching. A band at 1012 cm$^{-1}$ appears due to C−H in-plane bending. A band at 837−648 cm$^{-1}$ appears due to C−H out-of-plane bending. However, a band at lower than 600 cm$^{-1}$ is due to the interatomic vibration of silver metal.46

3.1.2. FESEM and EDS Analysis. For a morphological study, a FESEM analysis has been performed. The FESEM images at two different magnifications i.e., ×10000 and ×30000 are represented in Figure 4a,b, respectively, which indicate that the SNPs are highly agglomerated and have a small size in the solid phase; thus, the exact morphology of the SNPs cannot be confirmed from an FESEM analysis.

For elemental compositional analysis, an EDS profile was recorded, as shown in Figure 4c. A signal between the energies 2.70 and 3.35 keV indicates the presence of silver. Hence, the EDS profile confirms the formation of SNPs shown in Figure 4c. A prominent signal between 0.1 and 1.4 keV corresponding to an oxygen atom suggest that there might be formation of an Ag$_2$O phase along with SNPs, or the signal might also be due to the SiO$_2$ substrate on which the sample was drop-casted. Additionally, a signal near 0.1 keV was observed due to the presence of carbon atoms in the reducing agent as well as the stabilizing agent. A sharp signal between 1.4 and 2.7 keV was obtained due to coating of SNPs on the Si/SiO$_2$ substrate, and a pie chart containing the percentage weight composition of each element is shown in Figure 5d.

3.1.4. PXRD Analysis. The crystallite size and structure of the SNPs were obtained by PXRD, as shown in Figure 5. The three distinct diffraction peaks with 2θ values of 38.28, 44.32, and 65.92° can be assigned to the planes of (111), (200), and (220), respectively, as shown in Figure 5. The JCPDS file number 04-0783 indicates that the SNPs have a cubic crystal structure and are crystalline in nature.45,47 Also, the broadening of peaks obtained in the diffractogram shows the formation of SNPs, with the most intense peak being at 2θ = 44.32° for the (200) plane. However, a peak at 2θ equal to 55.17° (marked with an asterisk) is also obtained, which shows that the nanoparticles exist in the form of an Ag$_2$O phase and match with JCPDS file number 75-1532.35,48 The mean crystallite size of SNPs was calculated using the Debye−Scherrer equation (2)

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$

where $D$ is the average crystallite size, $\lambda$ is the X-ray wavelength, $\beta$ is the full width at half-maximum (fwhm), and $\theta$ is the diffraction angle. The fwhm corresponding to each Bragg peak is given in Table 2. It is found that the calculated average crystallite size is 17.76 nm.

3.1.5. TEM Analysis. For TEM analysis, a drop of the colloidal SNPs was deposited onto a TEM copper grid. After the copper grid dried, a TEM analysis was performed, and the

![Table 1. Rate Constants Observed in Different Experiments](https://doi.org/10.1021/acsomega.2c00046)
When the concentration of the silver ion was between 0.2 \times 10^{-3} M, such a small concentration of silver ions was not possible to agglomerate to an SNP colloid, and as a consequence, a kinetic study at this concentration in the range of 0.2 \times 10^{-3} M resulted in exponential growth due to formation of a gray precipitate that readily underwent agglomeration to form large-sized silver nanoparticles and created a hindrance in the growth kinetic study. Hence, a growth kinetic study at higher concentrations of silver ions for this reaction was not possible. The trend of rate constant for this reaction can be explained on the basis of the availability of hydroxide ions in the system. Initially, at a lower silver ion concentration, the amount of silver ions are not enough to react with all of the hydroxide ions, and hence following the absorbance at such a low concentration of silver ions is quite difficult. When the silver ion concentration is increased, a sufficient number of silver ions is present to react with hydroxide ions and also prevent the early-stage fast agglomeration process of silver ions. However, a few of the silver ions under alkaline conditions form silver oxide. This silver oxide supports the nucleation process, and when this surface becomes constant, the rate constant again starts falling. The existence of silver as silver oxide was also confirmed by EDS (see section 3.1.2) and PXRD studies (see section 3.1.4).

The effect of NaOH was studied between the range of 0.05 \times 10^{-3} to 0.4 \times 10^{-3} M with 0.2 \times 10^{-3} M [Ag^+], 0.6 \times 10^{-3} M [CTAB], and 0.2 \times 10^{-3} M [CTAB]. The exponential growth in absorbance with time for this variation is represented in dark yellow in the spectra shown in Figure 7a. The rate constant \( k_{\text{obs}} \) for the formation of the SNP colloid was calculated from the gradient of the plot of \( \ln(A_0 - A) \) versus time at a fixed absorption maximum of 410 nm under the same experimental conditions and is shown in Figure 7b. The rate constant for this reaction first increases and reaches a maximum when the concentration of hydroxide ions is in the range of 0.05 \times 10^{-3} to 0.3 \times 10^{-3} M. Afterward, the rate constant decreases with an increased concentration of hydroxide ion and becomes constant with the simultaneous formation of a slightly turbid SNP colloid. Due to the smaller number of hydroxide ions available in comparison to silver ions, no significant change was observed when 0.05 \times 10^{-3} and 0.1 \times 10^{-3} M NaOH were used. However, the rapid conversion of silver ions into silver oxide shows a noticeable change in the rate constant when 0.2 \times 10^{-3} M NaOH was used, and it was assumed that this silver oxide helps in the growth process of SNPs. It was believed that no SNP colloid formed in the absence of NaOH and also was observed that a minor concentration was enough to proceed with the reduction reaction of silver ions by NTA to produce the SNP colloid.

To study the effect of NTA on the rate of formation of the SNP colloid, a set of experiments was performed with 0.2 \times 10^{-3} M silver ions, 0.2 \times 10^{-3} M CTAB, 0.2 \times 10^{-3} M hydroxide ions, and NTA varied in the range 0.2 \times 10^{-3} \leq [NTA] \leq 1.2 \times 10^{-3} M. An exponential growth in absorbance was observed on plotting the graph between absorbance versus

### Table 2. PXRD Analysis Data

| \(2\theta\) (deg) | fwhm (rad) | average crystallite size \(D\) (nm) |
|-----------------|-----------|-----------------------------|
| 38.28           | 0.0086    | 12.6471                     |
| 44.32           | 0.0055    | 17.7614                     |
| 55.17           | 0.0102    | 7.7277                      |
| 65.92           | 0.0116    | 4.8426                      |
|                 |           | 10.7447 (mean)              |

images are captured at scales of 20 and 50 nm and represented in Figure 6a, b, respectively. A histogram is also plotted by an analysis of 43 particles, shown in Figure 6c. The spherical shape of the SNPs, as was supposed in FESEM analysis, was also confirmed by the TEM images. The average particle size obtained by the TEM histogram was in the range of 3–11 nm, and the average diameter of the SNPs was 6.22 ± 0.12 nm.

### 3.2. Growth Kinetic Study by Optimizing Different Experimental Parameters

The effect of \([Ag^+]\) on rate of SNP colloid formation was studied by varying its concentration in the range of 0.2 \times 10^{-3} to 0.4 \times 10^{-3} M with 0.2 \times 10^{-3} M [NaOH], 0.2 \times 10^{-3} M [CTAB], and 0.6 \times 10^{-3} M [NTA]. The change in absorption of the SNP colloid at the absorption maximum 410 nm (plasmonic band) with respect to time represented by a green line in spectra for the variation of [AgNO₃] resulted in exponential growth due to formation of the SNP colloid and is shown in Figure 7a. The rate constant \( k_{\text{obs}} \) for the formation of the SNP colloid was calculated from the gradient of the plot of \( \ln(A_0 - A) \) versus time at a fixed absorption maximum of 410 nm under the same experimental conditions, as represented by Figure 7b. A lower concentration of silver ions was not sufficient for its conversion to an SNP colloid, and as a consequence, a kinetic study at such a small concentration of silver ions was not possible.

When the concentration of the silver ion was between 0.2 \times 10^{-3} and 0.35 \times 10^{-3} M, the rate constants \( k_{\text{obs}} \) were found to be 2.127 \times 10^{-2}, 0.710 \times 10^{-3}, 0.383 \times 10^{-3}, and 1.360 \times 10^{-2}\ min^{-1} with regression coefficient values of 0.972, 0.970, 0.933, and 0.994, respectively. The trend observed in the rate constant was as follows; first, it started decreasing and reached a minimum and then increased. However, when the concentration of silver ion reached 0.4 \times 10^{-3} M, the rate constant again decreased and reached a value of 0.247 \times 10^{-3}\ min^{-1} with a regression coefficient of 0.968 and then became fixed for even higher concentrations of silver ions, which indicated that the rate of formation of SNP was independent of silver ion concentration. It should be noted that at a higher concentration of silver ions, i.e., 0.4 \times 10^{-3} \leq [AgNO₃] \leq 1.0 \times 10^{-3} M, the SNP colloid became turbid along with the formation of a gray precipitate that readily underwent agglomeration to form large-sized silver nanoparticles and created a hindrance in the growth kinetic study. Hence, a growth kinetic study at higher concentrations of silver ion for this reaction was not possible. The trend of rate constant for this reaction can be explained on the basis of the availability of hydroxide ions in the system. Initially, at a lower silver ion concentration, the amount of silver ions are not enough to react with all of the hydroxide ions, and hence following the absorbance at such a low concentration of silver ions is quite difficult. When the silver ion concentration is increased, a sufficient number of silver ions is present to react with hydroxide ions and also prevent the early-stage fast agglomeration process of silver ions. However, a few of the silver ions under alkaline conditions form silver oxide. This silver oxide supports the nucleation process, and when this surface becomes constant, the rate constant again starts falling. The existence of silver as silver oxide was also confirmed by EDS (see section 3.1.2) and PXRD studies (see section 3.1.4).

The effect of NaOH was studied between the range of 0.05 \times 10^{-3} to 0.4 \times 10^{-3} M with 0.2 \times 10^{-3} M [Ag^+], 0.6 \times 10^{-3} M [NTA], and 0.2 \times 10^{-3} M [CTAB]. The exponential growth in absorbance with time for this variation is represented in dark yellow in the spectra shown in Figure 7a. The rate constant \( k_{\text{obs}} \) for the formation of the SNP colloid was calculated from the gradient of the plot of \( \ln(A_0 - A) \) versus time at a fixed absorption maximum of 410 nm under the same experimental conditions and is shown in Figure 7b. The rate constant for this reaction first increases and reaches a maximum when the concentration of hydroxide ions is in the range of 0.05 \times 10^{-3} to 0.3 \times 10^{-3} M. Afterward, the rate constant decreases with an increased concentration of hydroxide ion and becomes constant with the simultaneous formation of a slightly turbid SNP colloid. Due to the smaller number of hydroxide ions available in comparison to silver ions, no significant change was observed when 0.05 \times 10^{-3} and 0.1 \times 10^{-3} M NaOH were used. However, the rapid conversion of silver ions into silver oxide shows a noticeable change in the rate constant when 0.2 \times 10^{-3} M NaOH was used, and it was assumed that this silver oxide helps in the growth process of SNPs. It was believed that no SNP colloid formed in the absence of NaOH and also was observed that a minor concentration was enough to proceed with the reduction reaction of silver ions by NTA to produce the SNP colloid.

To study the effect of NTA on the rate of formation of the SNP colloid, a set of experiments was performed with 0.2 \times 10^{-3} M silver ions, 0.2 \times 10^{-3} M CTAB, 0.2 \times 10^{-3} M hydroxide ions, and NTA varied in the range 0.2 \times 10^{-3} \leq [NTA] \leq 1.2 \times 10^{-3} M. An exponential growth in absorbance was observed on plotting the graph between absorbance versus

Figure 6. TEM image of SNPs at (a) 20 nm and (b) 50 nm. (c) Histogram plotted from the TEM image.
time and spectra shown in Figure 7a by the purple line. The rate constant ($k_{obs}$) for the formation of the SNPs colloid was calculated from the gradient of the plot of $\ln(A_{\infty} - A_t)$ versus time plots at a fixed absorption maximum of 410 nm under the same experimental conditions as represented in Figure 9d. There was a continuous change: i.e., a decrease—increase in the rate constant was observed. Also, it can be clearly seen from the data given in Table 1 that a small concentration of NTA was enough to reduce silver ions into SNPs. This decreasing—increasing behavior of the rate constant may be due to the accumulation of NTA on the SNPs surface. The presence of the $-\text{CONH}_2$ group is responsible for the adsorption of NTA by donating a lone pair of electrons through the nitrogen atom and hence producing nanosized silver particles. Finally, it was believed that NTA has the ability to form its hydrolysis product, i.e., nicotinic acid,\textsuperscript{42,50,51} on further addition of hydroxide ions, and hence the rate constant again starts falling.

To study the effect of an external stabilizer on the rate of formation of SNPs colloid, several sets of its concentration has been used in the range $0.1 \times 10^{-3} \leq [\text{CTAB}] \leq 0.6 \times 10^{-3}$ M, $0.2 \times 10^{-3}$ M [silver ion], $0.6 \times 10^{-3}$ M [NTA], and $0.2 \times 10^{-3}$ M [hydroxide ion]. An exponential growth in the absorbance was observed on plotting the absorbance versus time, shown in Figure 7a by the blue line. The rate constant ($k_{obs}$) for the formation of the SNPs colloid was calculated from the gradient of the plot of $\ln(A_{\infty} - A_t)$ versus time plots at a fixed absorption maxima of 410 nm under the same experimental conditions, as shown in Figure 7e. At lower concentrations i.e., $0.1 \times 10^{-3} \leq [\text{CTAB}] \leq 0.2 \times 10^{-3}$ M, the rate constant increases from $2.045 \times 10^{-2}$ to $2.127 \times 10^{-2}$ min$^{-1}$ with regression coefficients of 0.938 and 0.972,
respectively. As \([\text{CTAB}]\) is further increased to 0.3 \(\times 10^{-3}\) M, the rate constant becomes 1.210 \(\times 10^{-2}\) min\(^{-1}\) with a regression coefficient of 0.982, the rate constant increases to 1.635 \(\times 10^{-2}\) min\(^{-1}\) with a regression coefficient of 0.976, and then reaches a minimum value of the rate constant: i.e., 0.936 \(\times 10^{-2}\) min\(^{-1}\) at 0.5 \(\times 10^{-3}\) M [CTAB] with a regression coefficient of 0.986. The formation of a gray precipitate with turbidity in the reaction mixture was observed instead of a transparent SNPs colloid at [CTAB] \(\geq 0.6 \times 10^{-3}\) M. The stabilization of SNPs by CTAB was preferred over the self-stabilization of nanoparticles by the adsorption of NTA on its surface because there was practically no change in the intensity of the color and an absorption peak was observed after 60–90 days of the preparation. It is believed that the stabilization of SNPs by CTAB occurs according to an electrostatic mechanism. Thus, the stabilizing shell is not rigid and, hence, the effect of CTAB on the reaction mechanism can be ignored.

The overall reaction that actually takes place during the SNPs colloid formation is shown in eq 3 in Scheme 1. A simple and most plausible mechanism that is consistent with the employed experimental conditions is proposed and shown in Scheme 1. According to this mechanism, small-sized silver nanoparticles are formed through the reaction onto the surface of \(\text{Ag}_2\text{O}\). The formation of the \(\text{Ag}_2\text{O}\) surface in a basic medium is represented by eq 4 and is also supported by EDS and PXRD analyses. This \(\text{Ag}_2\text{O}\) surface helps the other silver ions to adsorb onto its surface and hence supports the nucleation process, with the formation of \(\text{Ag}_2\text{O}-\text{(Ag}^+\text{)}_n\), shown in eq 5. The adsorption of \(\text{Ag}_2\text{O}-\text{(Ag}^+\text{)}_n\) on the NTA through a nitrogen center is represented by eq 6. The species \(\text{Ag}_2\text{O}-\text{(Ag}^+\text{)}_n\) is then converted into \(\text{Ag}_2\text{O}\)-\(\text{(Ag}^-\text{)}_n\) as shown in eqs 7 and 8, which gains electrons through the nitrogen atom of the amide group. Then, the electron-rich species \(\text{Ag}_2\text{O}^-\text{(Ag}^-\text{)}_n\) was readily converted into electron-delocalized \(\text{e}^-\text{(Ag}_2\text{O)}\) species, represented by eq 9. Further, the electronically delocalized species helps in the growth process of SNPs shown in eq 10. Then a fast agglomeration of SNPs colloid was observed, i.e., the formation of large-sized silver nanoparticles, shown in eq 11, and they attract more attention, as they are supposed to be important intermediates in the photographic creation process. However, due to a fast hydrolysis the product obtained in eq 6 gets readily converted into nicotinic acid, as shown in eq 12 with the simultaneous release of ammonia gas.

### 3.3. Application of SNPs in the Catalytic Reduction of the Cationic Dye Methylene Blue (MB)

One of the major water pollutants coming from textile industries are the cationic dyes such as methylene blue (MB). It consumes the oxygen dissolved in water and aftermath endangers aquatic animals or systems. In the present work, we have tried to eliminate a lower concentration of MB by using SNPs as a catalyst. The reaction of catalytic reduction was followed by adding 5 mg of SNPs into 10 mL of 2 \(\times 10^{-3}\), 4 \(\times 10^{-3}\), and 6 \(\times 10^{-3}\) M ethanolic MB solutions (as shown in Figure 8a), and after the resulting mixture was set into the frame of a 3D orbital shaker for 1 and 24 h, a change in color of MB from blue to colorless was noticed (as shown in Figure 8b). The results obtained by monitoring the absorbance of the reaction mixture by a spectrophotometer after contact times of 1 and 24 h under the same experimental conditions are shown in Table 3.
control MB and that of the MB plus SNPs after a contact time of 1 and 24 h.

\[
\text{catalytic reduction} \% = \frac{A_0 - A_t}{A_0} \times 100
\]

(13)

The calculation of catalytic reduction corresponding to \(2 \times 10^{-3}\), \(4 \times 10^{-3}\), and \(6 \times 10^{-3}\) M MB in the presence and absence of SNPs is shown in Table 3. It can be concluded that a moderate catalytic reduction, i.e. 65–70%, could be observed when SNPs were in contact with the dye for 1 h. An enhanced catalytic reduction of up to 80–90% was noticed after a contact time of 24 h. The reaction involved in the catalytic reduction of MB is shown in Scheme 2. Therefore, SNPs

| concentration of control MB (10^{-3} M) | SNP dose (mg) | absorbance of control MB at adsorption of SNPs at 665 nm \( (A_0) \) | absorbance of MB after adsorption of SNPs at 665 nm \( (A_t) \) | catalytic reduction observed (%) |
|---|---|---|---|---|
| 2 | 5 | 0.34 | 0.1 | 0.07 | 70.58 |
| 4 | 5 | 0.77 | 0.25 | 0.09 | 67.53 |
| 6 | 5 | 1.19 | 0.42 | 0.15 | 64.70 |

Table 3. Summary of Data for Catalytic Reduction of MB Dye

Figure 9. SNP-dose-dependent absorption spectra after a contact time of 1 h: (a) \(2 \times 10^{-3}\) M MB; (b) \(4 \times 10^{-3}\) M MB; (c) \(6 \times 10^{-3}\) M MB. SNP-dose-dependent absorption spectra after a contact time of 24 h: (d) \(2 \times 10^{-3}\) M MB; (e) \(4 \times 10^{-3}\) M MB; (f) \(6 \times 10^{-3}\) M MB.
Scheme 2. Mechanism Involved in the Catalytic Reduction of MB by SNPs

synthesized by using NTA as a reducing agent can be an excellent eco-friendly approach for treating wastewater coming from industries: i.e., it can be successfully incorporated in the catalytic reduction of dyes.

4. CONCLUSION

The outcomes obtained from this study show that the existence of hydroxide ions enhanced the reduction of silver ions by nicotinamide to form a pinkish SNPs colloid. The 17.7614 nm sized crystallite SNPs having an average diameter of 6.22 nm are well stabilized due to the presence of CTAB in the medium. From a growth kinetic study, we showed that the reduction of silver ions proceeded through the formation of silver oxide in colloidal form upon reaction with hydroxide ions and to some extent due to the subjection of UV light. Further, NTA is oxidized by the silver ions adsorbed on the silver oxide surface and then readily undergoes hydrolysis to form nicotinic acid as a hydrolysis product with the release of ammonia gas. SNPs prepared by NTA can be a good catalyst for reducing MB dye to overcome the wastewater treatment problem of textile industries. To the best of our knowledge, this is the first time a growth kinetic study of SNPs using NTA as a reducing agent has been reported.

■ AUTHORIZING INFORMATION

Corresponding Author
Radhey Mohan Naik — Department of Chemistry, Lucknow University, Lucknow 226007 Uttar Pradesh, India; orcid.org/0000-0003-1782-9125; Email: radheynaik@gmail.com

Authors
Indresh Kumar — Department of Chemistry, Lucknow University, Lucknow 226007 Uttar Pradesh, India
Chinky Gangwar — Department of Chemistry, Lucknow University, Lucknow 226007 Uttar Pradesh, India
Bushra Yaseen — Department of Chemistry, Lucknow University, Lucknow 226007 Uttar Pradesh, India
Pradeep Kumar Pandey — Department of Chemistry, Lucknow University, Lucknow 226007 Uttar Pradesh, India
Sheo K. Mishra — Department of Physics, Indira Gandhi National Tribal University, Amarkantak 484887 Madhya Pradesh, India

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.2c00046

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