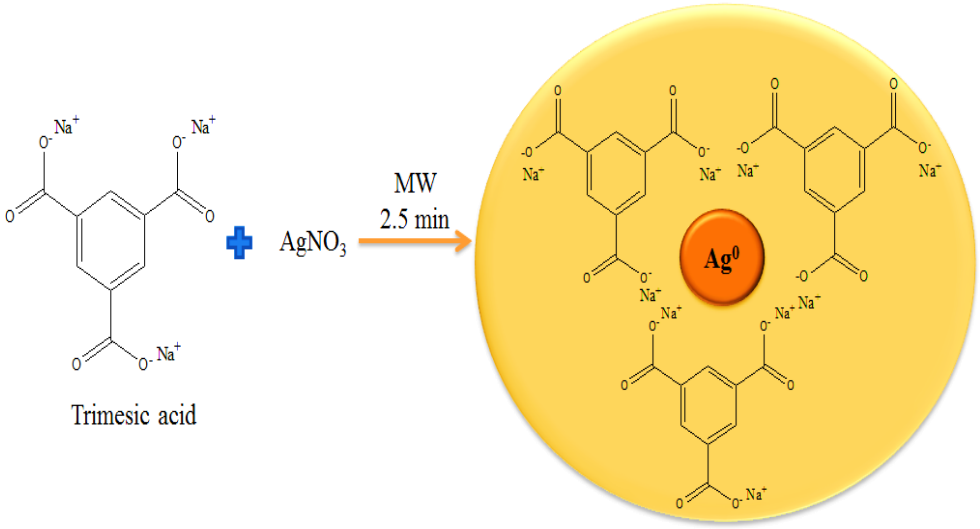
Chapter 5

a) Microwave Synthesis of Trimesic acid capped silver nanofluids for Catalytic Applications



5a.1 Introduction

Nanofluid (NF) is a form of stable colloidal pseudo-homogeneous phase system comprising of metal nanoparticles in some base fluid (Li et al., 2017) which have received attention due to their satisfactory dispersion stability with increased surface area resulting in improved mass transfer, increased adsorption, viscosity properties and applications in heat transfer and catalysis. They are liquid suspensions of nanoparticles with at least one of their principal dimensions smaller than 100 nm. In comparison to base fluids like oil or water, nanofluids have been found to have improved thermophysical properties such as thermal conductivity, thermal diffusivity, viscosity and convective heat transfer coefficients (Wong & Leon, 2010).

Nanofluids can be used in a wide range of engineering applications, including those in the medical field (Habeeb & Majdi, 2019), the power plant cooling system (Malek et al., 2018), computers (Habeeb & Majdi, 2019), catalysis (Mannu et al., 2021) and the automotive industry (Dey & Sahu, 2021). They are considered to be next-generation of heat transfer fluids (Jama et al., 2016). (Figure 5a.1).

For the synthesis of noble-metal colloids, usually solvents with high boiling points such as ethylene glycol (EG) or oleylamine are applied. Alkaline EG functions as a solvent and reducing agent,and the reaction products stabilize the NPs (Neumann et al., 2017) whereas water as the solvent requires surfactants, for example, glucose, to stabilize the NPs (Comotti et al., 2004).

There is a recent report on synthesis of nanofluid formulations wherein silver nanoparticles were loaded on Alumina/Silica and dispersed in water as base fluid. The NF was used as catalyst for nitrophenol reduction (Mannu et al., 2021). In other report, copper nanofluids were developed using microwave energy (H. Zhu et al., 2004).

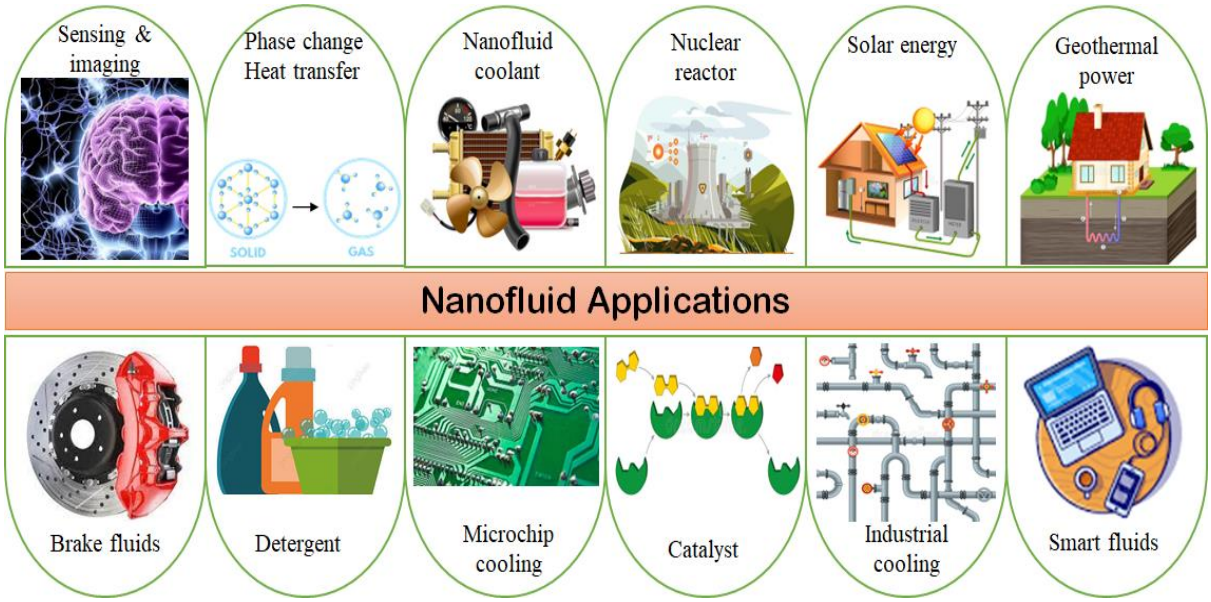


Figure 5a. 1. Application of nanofluids

Synthesis of nano fluids

The first step in conducting experimental research on nanofluids is the preparation of the nanofluids. The one-step preparation and the two-step preparation processes are the two main ways to prepare nanofluids (Journals, 2017) (figure 5a.2).

1. One-step method

In this method, physical vapor deposition technique is used to form a stable nanofluid. The direct evaporation and condensation of nanoparticles take place in the base fluid (A. R. I. Ali & Salam, 2020).

Advantages: The nanoparticle agglomeration is minimized. The pure and uniform nanofluids can be formed.

Disadvantages: The fluids with low vapour pressure are compatible with this method. Moreover, residual reactants are left in the nanofluid. The cost of the process is high.

2. Two-step method

The first step of this two-step method is to obtain nanoparticles by different methods. Then in the second step, these nanoparticles are dispersed into the base fluid to get desired nanofluid.

Advantages: Most economic method for large scale production

Disadvantages: Aggregation of nanoparticles occurs. To overcome this, surfactant is used for the stability (A. R. I. Ali & Salam, 2020).

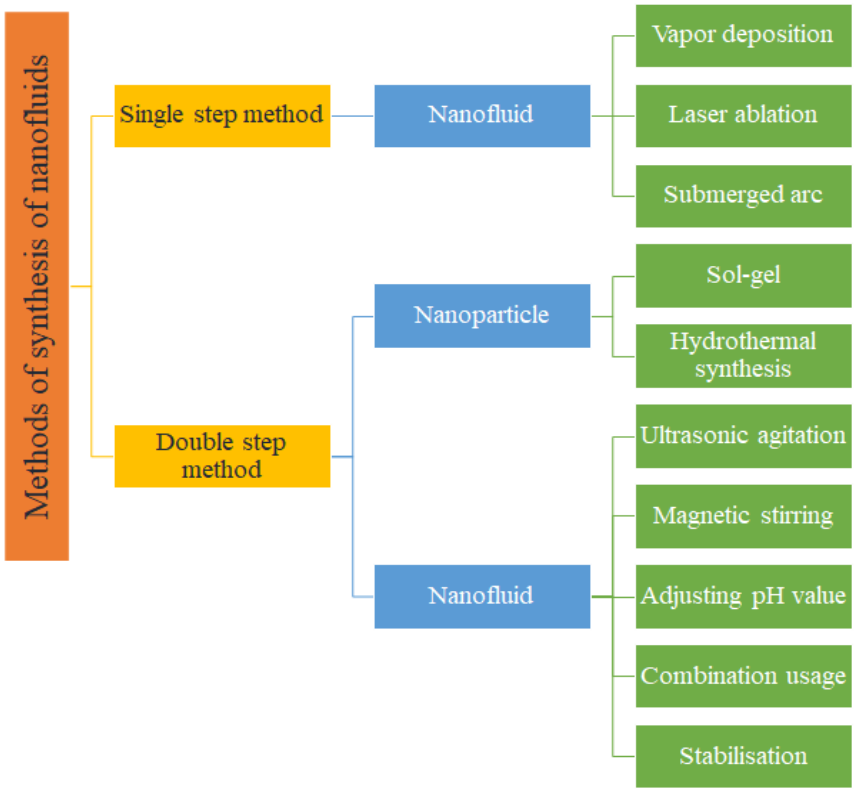


Figure 5a. 2. Methods of synthesis of nanofluids (H. M. Ali et al., 2018)

The most practical way to get rid of nitrophenols is to use a catalyst to turn it into 4-Aminophenol (4-AP) (Murugan & Jebaranjitham, 2012). There is growing interest in this technique for removing nitroaromatic chemicals (Cárdenas-Lizana et al., 2012)(Coccia et al., 2012). It is a green procedure (Jianming Zhang et al., 2013)(Jun Zhang et al., 2018) devoid of organic solvents. Additionally, aromatic amines are commonly used in products utilized as stepping stones in the manufacturing of colours, drugs and agrochemicals (Rajagopal & Spatola, 1995).

The conventional techniques for reducing these nitro compounds, however, call for the employment of reagents like Raney Ni in the presence of acid (CROSSLEY, 1922)(Nadagouda et al., 2011). As a result, the procedure is not green, but rather pricy and hazardous to the environment. Using $NaBH_4$ in water as the hydride source is a cleaner alternative, however nitro group reduction with $NaBH_4$ in the absence of a catalyst takes time.

The use of non-supported metal colloids has attracted attention as green catalysts at the frontier between homogeneous and heterogeneous catalysis. This is due to the ease of their preparation and high catalytic performances resulting from facile access of reactants to the nanoparticle surfaces (Astruc, 2020).

Narayan Pradhan et. al. synthesized silver metal colloids as full growing microelectrode (Journals, 2017) . They observed that the growing particles are more catalytic than bulk metal. With the use of catalytic quantity of this silver metal colloids in combination with $NaBH_4$, they have done reduction of nitro compounds like 2-nitrophenol, 4-nitrophenol and 4-nitroaniline. According to them, strong contact between the substrate and the catalyst surface has been found to be necessary for efficient catalysis. If the catalyst surface is susceptible to oxidation, this type of contact could lead to poisoning.

It was found that smaller AgNPs often displayed better activity during reduction catalysed by Ag because of a more favourable negative redox potential and a higher surface-to-volume ratio that enabled electron transport from the surface of AgNPs to reactants (Mori et al., 2009)(Z. Zhang et al., 2012). However, when used as catalysts, tiny AgNPs tend to aggregate, reducing the surface area of the catalyst (Cañamares et al., 2005)(Hu et al., 2015). To address this disadvantage, capped colloidal AgNPs dispersion was used (Yang et al., 2013). However, this lowered the catalytic activity by passivating parts of the AgNP surface-active sites. Additionally, it was challenging to extract and recycle the highly dispersed AgNPs (P. Zhang et al., 2011).

DTPA capped silver nanofluids in water have been used as sensors for detection of chromium species (Bhatt et al., 2018). Nanofluids supported on Al_2O_3 have been used as catalysts for the removal of 4- nitrophenol (Mannu et al., 2021). Cu–Ag and Au-Ag based bimetallic nanoparticle nanofluids have been used for heat transfer and catalytic reduction of 4 nitrophenol (Dsouza et al., 2021).

In the present work we have prepared stable AgNF using Benzene tricarboxylic acid (BTC) as stabilizer with the help of microwave energy. The catalytic potential of Ag-BTC NF has been investigated for reduction of model aromatic nitro compounds to their respective amino compounds.

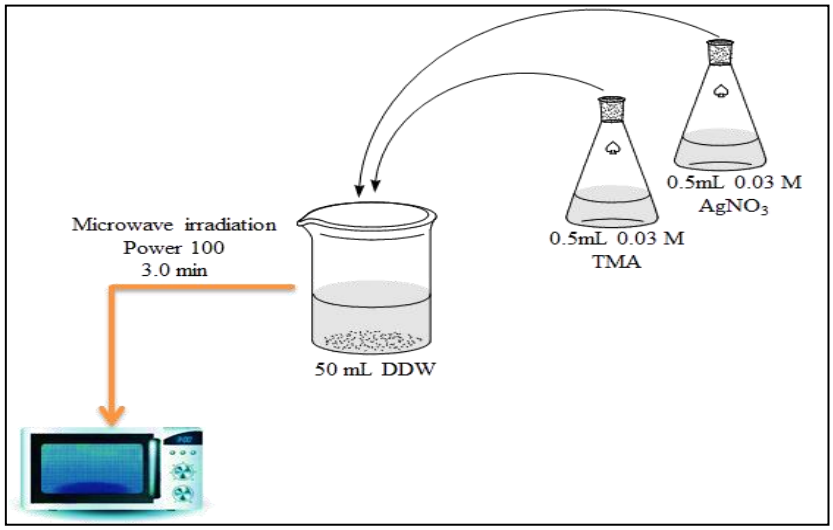
5a.2 Materials and methods

5a.2.1 Materials

Silver nitrate (Spectrochem; 99.9%), Trimesic acid/Benzene tricarboxylic acid (BTC) (Sigma aldrich), were used in this study without further purification. Microwave make ONIDA (1200W, 2450 MHz) was used for the synthesis of nanoparticles.

5a.2.2 Microwave synthesis of Ag-BTC NF

AgNF synthesis was carried out by mixing 0.5 mL of 0.03 M $AgNO_3$ solution and 0.5 mL of 0.03 M Trimesic acid/Benzene tricarboxylic acid (BTC) (prepared in 0.2 M NaOH) in 50 mL conductivity water. The solution was then irradiated under 100 W power in microwave oven for 120 seconds. The colour change from colourless to yellowish-brown indicated the formation of AgNF. The resultant solution is diluted to 50 mL and used further for experiments and characterization.



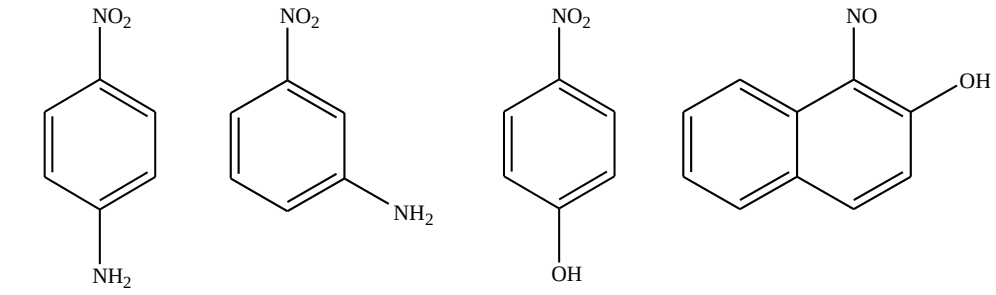
5a.2.3 Characterization of silver nanofluid

The synthesized AgNF was characterized by UV visible spectral analysis using UV visible spectrophotometer make JASCO V-630 at wavelength of 200-800 nm. Size, shape and crystallinity of AgNF were examined using Transmission electron microscope make Philips CM 200. Raman spectroscopy analysis was used to confirm the functional groups present using Micro Raman model STR 500 (Atrix corporation with) Nd-YAG laser (785 nm wavelength).

5a.2.4 Catalytic experiments

The catalytic activity of Trimesic acid capped AgNF was examined by reduction of nitro derivatives (p-Nitroaniline (p-NA), m-Nitroaniline (m-NA), p-Nitrophenol (p-NP)) and Nitroso derivative, 1-Nitroso-2-naphthol (NN) into their respective amino derivatives using $NaBH_4$ and AgNF. The structures of nitro and nitroso derivatives investigated are given in figure 5a.3. In a typical experiment, 0.2 mL of 100 ppm of the nitro compound was diluted to 2 ml and transferred into cuvette then 0.2 ml of 0.1 M $NaBH_4$ was added. Thereafter, 0.2 mL of AgNF solution was added to evaluate the catalytic reduction of nitro compounds. The

progress of the reactions was monitored at 1 minute intervals using UV–visible spectrophotometer.



p-Nitroaniline m-Nitroaniline p-Nitrophenol 1-Nitroso-2-naphthol

Figure 5a. 3. Chemical structures of nitro compounds

5a.2 Results and Discussion

5a.2.1 Characterization of AgNF

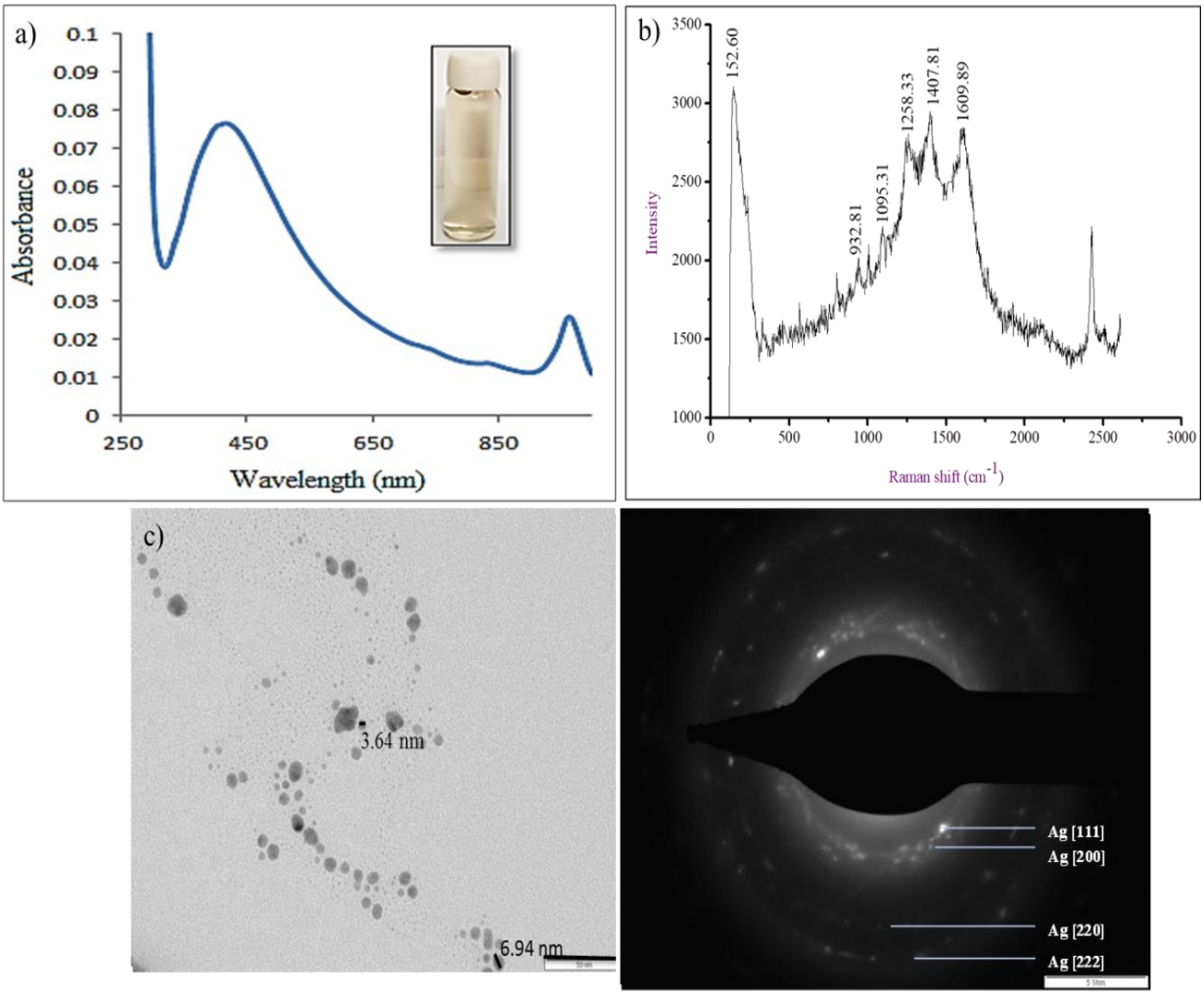


Figure 5a. 4. (a) UV spectra of AgNF; (b) Raman spectra of Ag-BTC NF; (c) TEM and SAED images of Ag-BTC nanofluid

Due to the surface plasmon resonance phenomenon, AgNF absorbs in the visible region (W. Zhu et al., 2014). On addition of trimesic acid to silver nitrate solution, a visible colour change (appearance of a yellowish-brown colour) was observed. This is indicative of formation of AgNF. From UV–Vis spectra of the Ag nano fluid shown in figure 5a.4(a), it was observed that the SPR peak appeared at 440 nm characteristic of silver nanoparticles and at 900 nm in the near IR region which is attributed to SPR of non-spherical particles (Dong et al., 2014; Ider et al., 2017). The average hydrodynamic size of silver nanoparticles in AgNF was observed to be 128.6 nm.

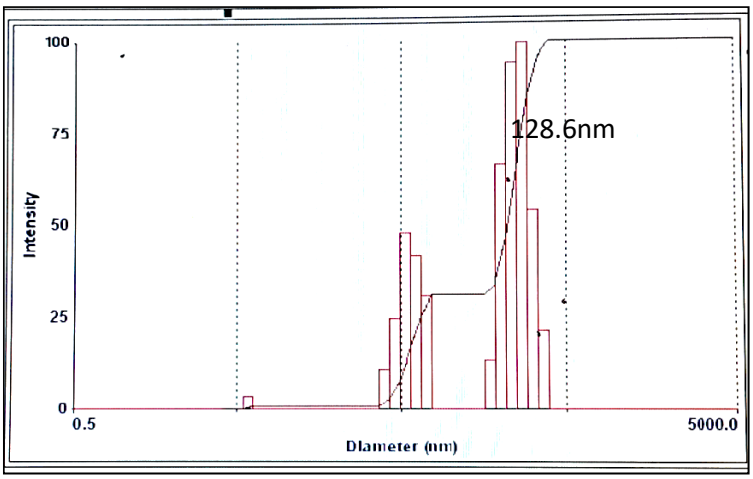


Figure 5a. 5 DLS spectra of Ag-BTC

TEM images of Ag nanofluid and the SAED pattern depicted in figure 5a.4(c) indicated the particles to be pseudospherical and ellipsoidal. The SAED pattern depicted the cluster of minute crystals of Ag mainly oriented in the (111) plane with FCC geometry. From the figure 5a.4(c), the calculated size of the pseudo spherical AgNPs was approximately 3.64 nm.

Raman spectra of the silver nanofluid as shown in figure 5a.4(b) exhibited a strong peak at 152.60 cm^{-1} which may be attributed to the stretching vibrations of Ag-O bonds (Kora et al., 2012) indicating the formation of an ionic bond between silver and carboxylate group of trimesic acid. The peak at 1407.81 cm^{-1} was attributed to the symmetric stretch of carboxylate group (Kizil et al., 2002) while the peak at 1609.89 cm^{-1} resulted from the asymmetric stretching mode of ionized carboxylate groups. The peak observed at 932.81 cm^{-1} may be attributed to C-C stretching, CH in-plane bending and deformation modes respectively.

5a.2.2 Catalytic activity of Ag nanofluid

The catalytic activity of Ag-BTC NF for the reduction process was monitored by UV- visible spectroscopy. The time dependent UV–Vis responses and kinetics plots for p-nitroaniline, m-nitroaniline, p-nitrophenol and 1- nitroso 2 naphthol are shown in figure 5a.6(a) to 5a.6(d).

The conversion from nitro to amino occurs via an intermediate phenolate ion formation in case of p-Nitrophenol and 1-Nitroso-2-napthol. The p-Np exhibited maximum absorbance at ~317 nm, which exhibits a red shift to 400 nm in the presence of $NaBH_4$ due to the formation of 4-nitrophenolate ion in the alkaline medium caused by $NaBH_4$. On addition of NF, there was decrease in the intensity of the absorption peak at 400 nm and appearance of a new peak at 298 nm indicating the formation of reduction product, p-amino phenol. A similar observation was made in case of 1-Nitroso-2-napthol where the absorbance maxima at 375 nm was observed to red shift to 290 nm confirming the formation of m-Phenylenediamine while a redshift from 374 to 315 nm and 375 to 290 nm was observed in case of p-Nitroaniline and m-Nitroaniline respectively.

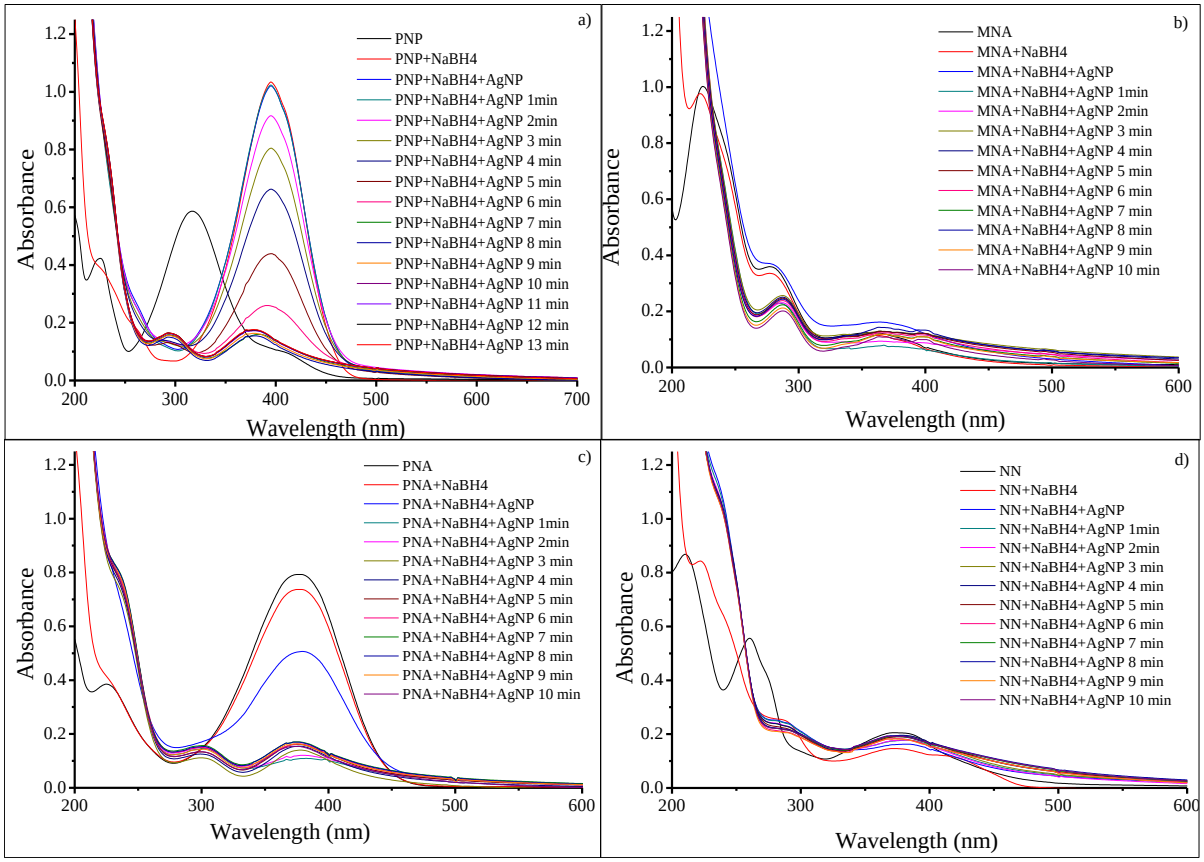


Figure 5a. 6. UV–Vis spectra acquired during reduction in the presence of Ag-BTC NF of (a) p-nitrophenol; (b) m-Nitroaniline; (c) p-Nitroaniline; (d) 1-Nitroso-2-napthol

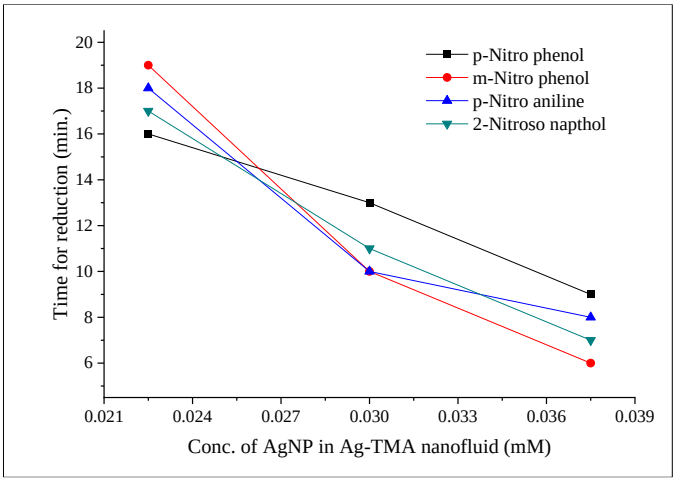


Figure 5a. 7 effect of concentration of Ag-BTC NF on the reduction time.

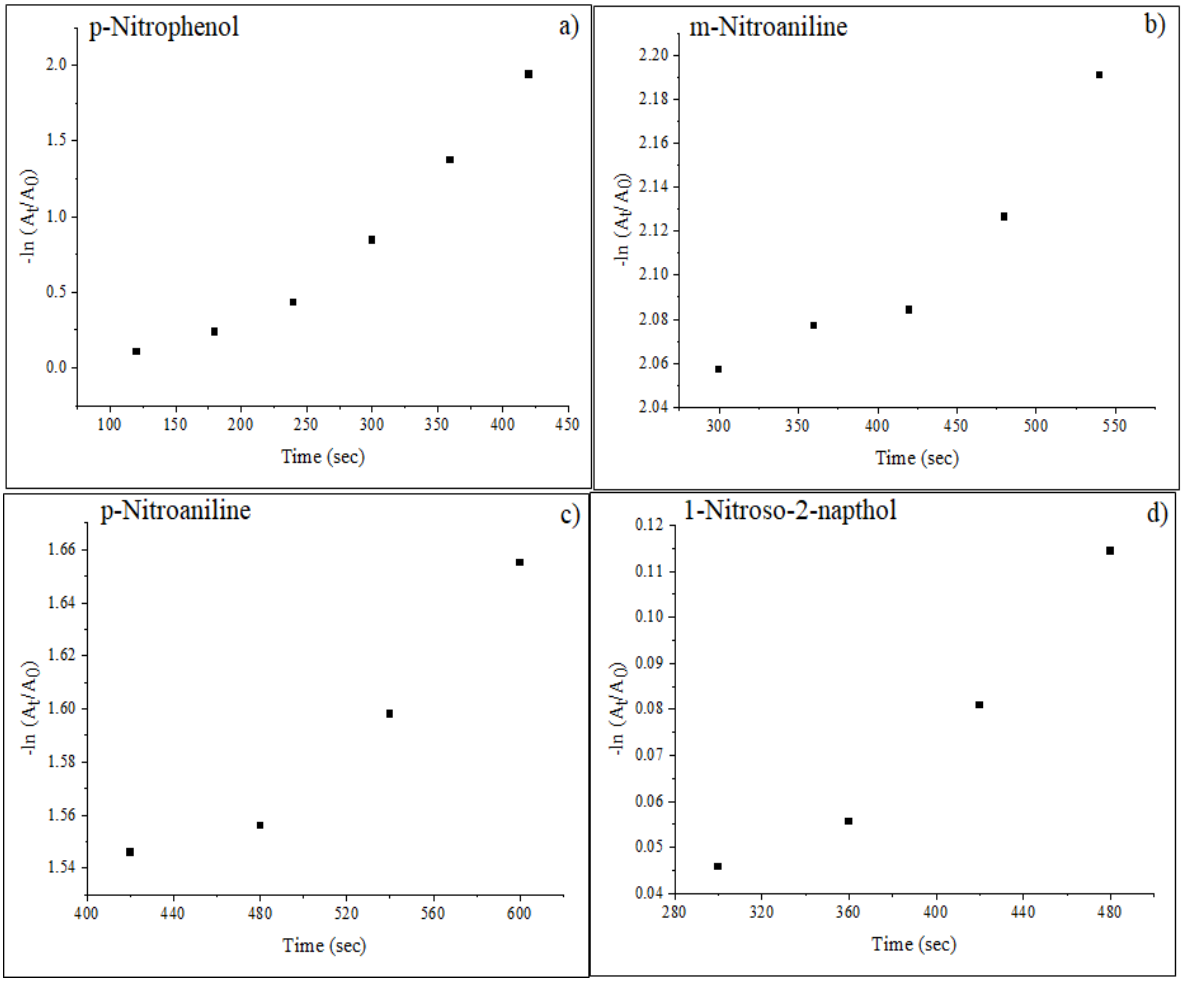


Figure 5a.8. Reduction kinetics of (a) p-nitrophenol; (b) m-Nitroaniline; (c) p-Nitroaniline; (d) 1-Nitroso-2-napthol.

To check the effect of Ag-BTC dose on reduction kinetics, the time for reduction was measured by UV spectroscopy taking 0.0225 mM, 0.03 mM and 0.0375 mM of the catalyst

solution (figure 5a.7). From the spectra it was observed that the time for reduction decreased as the catalyst dose increased.

The reduction of p-nitrophenol, o and p-nitroaniline and 1-nitroso-2-naphthol using $NaBH_4$ in the presence of metal nanoparticles followed pseudo-first-order kinetics. The rate of reduction for the model reactants under study has been observed to follow the sequence p-nitrophenol, m-Nitroaniline, p-Nitroaniline, 1-Nitroso-2-napthol with rate constants 8.41×10^{-3}, 8.91×10^{-4}, 9.54×10^{-4}, 5.59×10^{-4} sec^{-1} as seen from figure 5a.8. The rate constants of the reaction were found to be comparable to literature reported silver-based catalysts as seen from Table 5a.1.

Table 5a. 1. Rate constants of literature reported catalysts for degradation of various nitro pollutants:

p-Nitrophenol		
Ag-SiO_2 NP	6.02×10^{-3}	(M. et al., 2021)
Au–Ag bimetallic NP	47.88	(Meena Kumari et al., 2015)
Silver nanoparticles from the Psidium guajava leaf extract.	9.54	(Kaur et al., 2019)
Ag–γ-Fe_2O_3	1.44×10^{-3}	(Sallam et al., 2018)
o-Nitroaniline		
Ag-NP synthesized using Tamarindus indica seed coat extract	2.43×10^{-3}	(Edison et al., 2016)
Ag–γ-Fe_2O_3	0.904×10^{-3}	(Sallam et al., 2018)
p-Nitroaniline		
Ag-NP synthesized using Tamarindus indica seed coat extract	6.22× 10-3	(Edison et al., 2016)

5a.3 Conclusions and further work

In this work, Ag-BTC NF was successfully prepared by microwave irradiation. The carboxylate anions of trimesic acid coordinated to the metal surface and aided in stabilization of silver and reduction under microwave energy. The duration of irradiation and power of microwaves influenced the formation of silver nanoparticles. Ag-BTC NF exhibited characteristic absorbance peaks at 440nm and 900 nm. Structural examination unveils their pseudo-spherical and ellipsoidal nature and the crystals of Ag are in FCC geometry (111). The Ag-BTC NF has ability to act as pseudo homogeneous catalyst for various organic transformations where it acts as reducing agent. The rate constants of reduction for p-nitrophenol, m-Nitroaniline, p-Nitroaniline, 1-Nitroso-2-napthol are 8.41×10^{-3}, 8.91×10^{-4},

9.54×10^{-4}, 5.59×10^{-4} sec^{-1} respectively. The rate constants of the reaction were found to be comparable to literature reported on silver-based catalysts. Work is in progress for the preparation of magnetic Ag-BTC to achieve recyclability of the catalyst.

5a.4 References

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