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# Dendrimer encapsulated Silver nanoparticles as novel catalysts for reduction of aromatic nitro compounds

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**Abstract.** Polyethylene glycol (PEG) core dendrimer encapsulated silver nanoparticles (AgNPs) were synthesized through normal chemical reduction method, where dendrimer acts as reducing and stabilizing agent. The encapsulated AgNPs were well characterized using TEM, DLS and XPS techniques. The synthesized AgNPs showed excellent catalytic activity towards the reduction of aromatic nitro compounds with sodium borohydride as reducing agent and the results substantiate that dendrimer encapsulated AgNPs can be an effective catalyst for the substituted nitro aromatic reduction reactions. Also the kinetics of different nitro compounds reductions was studied and presented.

## 1. Introduction

Nanoparticles of noble metals have attracted lot of attention of researchers in recent times due to its large surface-volume ratio and smaller in size which will alter its physical and chemical properties tremendously [1]. Among the metal nanoparticles studied, silver nanoparticles (AgNPs) have found suitable for applications in catalysis [2-4], surface-enhanced Raman scattering studies, [5,6] photographic processes [7-9] and fluorescence studies. Till date, many reducing agents have been tried out to synthesize metal nanoparticles such as hydrazine, sodium borohydride and DMF and environmentally friendly ethylene glycol. The polymer of ethylene glycol, polyethylene glycol, has been extensively used in pharmaceutical and biomedical industries as prodrug [10]. Dendrimer encapsulated nanoparticles are considered as good candidates for different applications owing to their unique properties and are particularly in catalysis [11,12].

Environmental pollution due to industrial effluents is great concern worldwide as it has severe impact on human health [13]. 4-Nitrophenol (4-NP), a major pollutant as per US EPA due to its adverse effects such as skin/eye irritation and also affect liver, kidney and central nervous system intensively and hence reducing 4-NP is an absolute necessity. The reduction product 4-aminophenol (4-AP) has several applications in pharmaceutical industries as intermediate in synthesis analgesic and antipyretic drugs [14]. In addition it can also be used as photographic developer, corrosion inhibitor in paints and anticorrosion-lubrication agent in fuels. It is also used as a wood stain and dyeing agent for fur and feathers [15]. Reductions of nitro compound using various metal nanoparticles are reported over the decades [16-21]. Mostafav *et.al.*, reported the AgNPs as *in situ* active catalyst towards reduction of 4-nitrophenol, 2-nitrophenol and 4-nitroaniline[22]. Recently, copper-silver (Cu-Ag) mixed nanoparticles on the surface of pure cellulose acetate [23] and metallogel of iron-carboxylates [24] were prepared and used as the catalyst for the reduction of nitro-arenes. Reduction of 4-NP with NaBH<sub>4</sub> in the presence of dendrimer encapsulated AgNPs has been earlier published by the authors of



this article [25]. In the present work, synthesized dendrimer encapsulated AgNPs were tried out as catalysts for the reduction of different substituted aromatic nitro compounds.

## 2. Experimental

### 2.1. Materials

2-Hydroxy-5-nitrobenzyl bromide from Fluka, sodium borohydride, 4-nitrophenol, 4-nitroaniline, dichloromethane (DCM), 4-nitrocatechol, sodium chloride (NaCl), sodium sulphate (Na<sub>2</sub>SO<sub>4</sub>), sodium nitrate (NaNO<sub>3</sub>), 5-Hydroxy-2-nitrobenzaldehyde and other reagents procured from SRL Chemicals, India were used in the present study.

### 2.2. Synthesis of dendrimer encapsulated AgNPs

Synthesis of PEG dendrimer was carried out in a three step method as described in an earlier publication [26]. Dendrimer encapsulated AgNPs were prepared using a procedure similar to the one reported [27]. It involves *in situ* preparation of AgNPs by dissolving hydroxyl terminated dendrimer in double distilled water followed by addition of silver nitrate and heating it at 80°C for 1 h with vigorous stirring and finally cooling to room temperature resulting in a pale pink coloured solution. The prepared dendrimer was characterized using NMR, MALDI TOF while the encapsulated AgNPs were characterized using TEM, XPS, DLS and UV-Visible spectroscopic techniques and reported in our earlier publication [25].

### 2.3. Catalytic Reduction of substituted nitro compounds

The reduction processes of substituted nitro compounds namely, nitrobenzene, 4-nitrotoluene, 4-nitrobenzaldehyde, 4-nitroaniline, 4-nitrocatechol, 5-hydroxy-2-nitrobenzaldehyde, 2-hydroxy-5-nitrobenzyl bromide was carried out in the presence and absence of dendrimer encapsulated AgNPs using NaBH<sub>4</sub> as the reducing agent. Effect of concentration of the reducing agent during the reduction processes was also studied. Details of the shift in absorption when the compounds are reduced from phenol to phenolate ion and then to amino compounds, catalyzed by dendrimer encapsulated AgNPs are given in Table 1.

Kinetics of the reduction processes was monitored in the presence and absence of catalyst. The concentration of NaBH<sub>4</sub> maintained was far in excess compared to the concentration of substituted nitro compounds as well as the catalyst and hence the kinetics of the reaction was monitored using pseudo-first order model.

## 3. Results and discussion

The reduction processes was followed on Shimadzu UV-Visible spectrophotometer. The initial yellow colour of the nitro compounds gradually diminished and the solutions became colourless indicating the reduction of nitro group to amino group in the presence of NaBH<sub>4</sub> and the catalyst, which was evidenced by the gradual decrease in the absorbance intensities corresponding to aromatic nitro compound and appearance and gradual growth of the peak corresponding to the amino compound when scanned between 190 and 600 nm. It was observed that without the catalyst, the reaction could proceed till the formation of phenolate ion only, immediately on addition of NaBH<sub>4</sub>, as indicated by the deepening of the yellow colour of the nitro compounds and shift in the characteristic absorption peak to higher wave length but complete reduction of the nitro group to amino group was not occurred in the absence of the catalyst, even after 24 h. As presented in table 1, formation of phenolate ion was noticed in compounds containing –OH group while phenolate ion formation was not noticed in the other compounds.

In the presence of as synthesized dendrimer encapsulated AgNPs as catalyst during the reduction process, the reaction proceeded within a maximum duration of 90 minutes for conversion to amino compounds confirming that both reducing agent and catalyst are necessary for the reduction to proceed to completion. Kinetic rates of the reduction to amino compounds were studied using a

pseudo first order kinetic model and the rate constants (k) value was determined from the log [A] vs. time plots are shown in the Table 2. The rates of the reduction processes were found to increase with increase in concentration of NaBH<sub>4</sub> (20-100 fold increase in rate was observed when NaBH<sub>4</sub> concentration was increased from  $2 \times 10^{-3}$  to  $1 \times 10^{-2}$  mol dm<sup>-3</sup>). A comparison of the reduction of nitro compounds show that the reduction rate follows the order, 4-nitrobenzaldehyde (4-NB) > nitrobenzene (NB) > 4-nitrocatechol (4-NC) > 4-nitroaniline (4-NA) > 5-hydroxy-2-nitrobenzaldehyde (5-OH-2-NB) > 4-nitrotoluene (4-NT) > 2-hydroxy-5-nitrobenzylbromide (2-OH-5NBB). The observed catalytic activity with our reported nanocatalyst is comparable with or better than the recent reports on catalytic reduction of nitro compounds [28,29].

Table 1: Shift in  $\lambda_{\max}$  during the reduction of nitro compound

S.No.	Compound	$\lambda_{\max}$ of the nitro compound (nm)	Observed $\lambda_{\max}$ for phenolate ion formation (nm)	Observed $\lambda_{\max}$ for amino compound formation (nm)
1.	#4-Nitrophenol	377	400	300
2.	*4-Nitroaniline	380	380	300
3.	4-Nitrocatechol	385	420	300
4.	2-OH-5NBB	320	408	305
5.	5-OH-2-NB	358	418	**
6.	*4-Nitrobenzaldehyde	286	286	237
7.	*Nitrobenzene	267	267	230
8.	*4-Nitrotoluene	288	288	237

\*Indicates that phenolate ion is not formed during the reduction process.

\*\* Peak for amino compound could not be located because of merger of the peak with peak of parent compound.

#Data taken from our previous report [23].

The reduction rate is observed to get affected mainly due to presence of primary substituent in the benzene ring. From the above order, it could be reasonably inferred that the electron withdrawing groups in the benzene ring facilitate the reduction whereas the electron donating groups impede the reduction reaction. When compared with the reported Hammett values ( $\sigma$  and  $\rho$ ) [30] of the substituents present in the different aromatic nitro compounds, the observed trend above is considered possible.

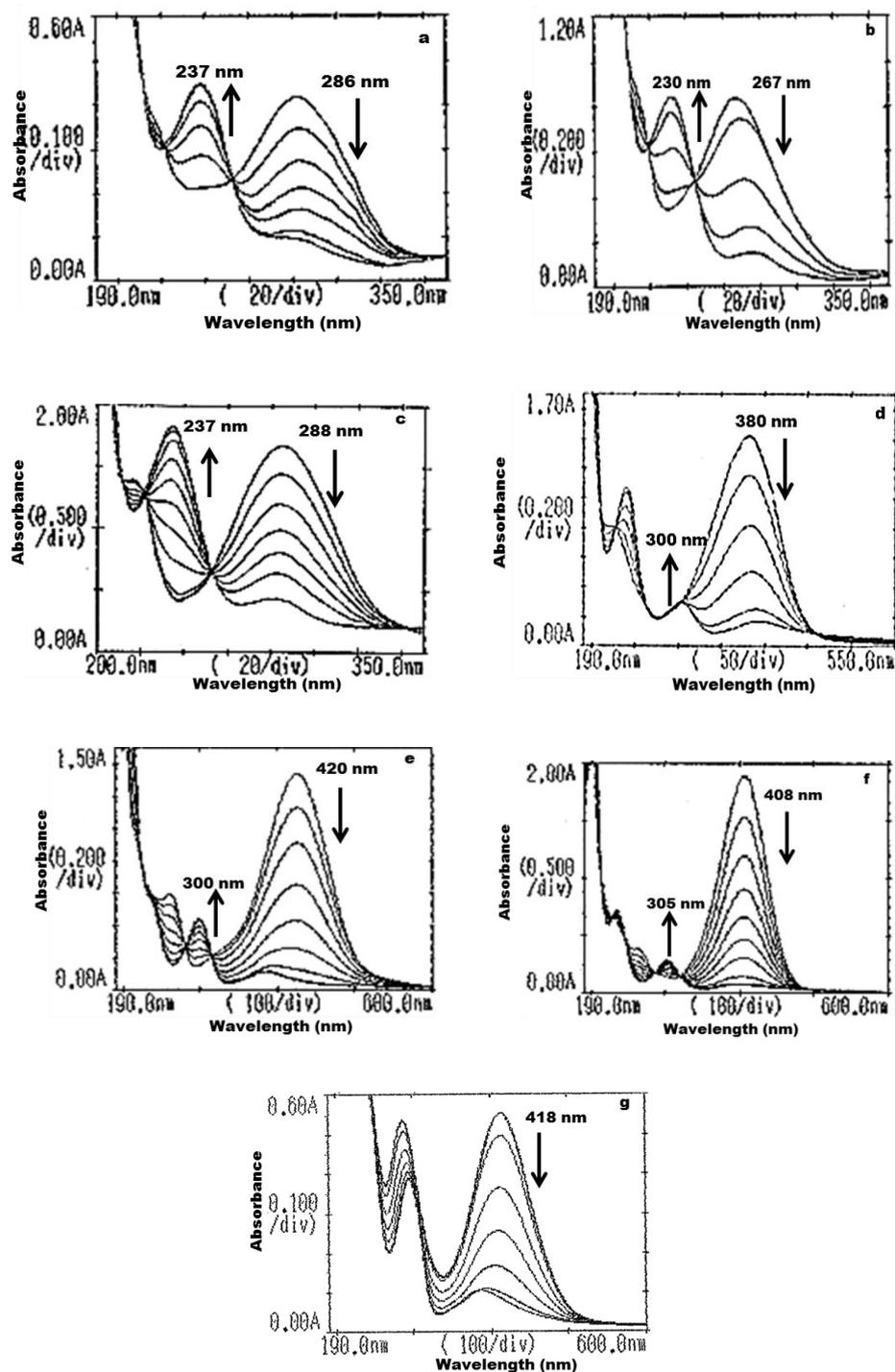


Fig. 1: Kinetics of the reduction of nitro compounds using  $\text{NaBH}_4$  as reductant in the presence of nano-Ag as catalyst a) 4-Nitrobenzaldehyde b) Nitrobenzene c) 4-Nitrotoluene d) 4-Nitroaniline e) 4-Nitrocatechol f) 2-hydroxy-5-nitrobenzyl bromide g) 5-hydroxy-2-nitrobenzaldehyde.

Table 2: Data on kinetics of reduction of different substituted aromatic nitro compounds catalysed by dendrimer encapsulated AgNPs

[NaBH <sub>4</sub> ] / 10 <sup>-3</sup> mol dm <sup>-3</sup>	[4-NB] k <sub>obs</sub> / 10 <sup>-3</sup> , s <sup>-1</sup>	[NB] k <sub>obs</sub> / 10 <sup>-3</sup> , s <sup>-1</sup>	[4-NT] k <sub>obs</sub> / 10 <sup>-3</sup> , s <sup>-1</sup>	#[4-NP] k <sub>obs</sub> / 10 <sup>-3</sup> , s <sup>-1</sup>	[4-NA] k <sub>obs</sub> / 10 <sup>-3</sup> , s <sup>-1</sup>	[4-NC] k <sub>obs</sub> / 10 <sup>-3</sup> , s <sup>-1</sup>	[2-OH-5- NBB] k <sub>obs</sub> / 10 <sup>-3</sup> , s <sup>-1</sup>	[5-OH- 2NB] k <sub>obs</sub> / 10 <sup>-3</sup> , s <sup>-1</sup>
1.0	-	0.61	-	-	-	-	-	-
2.0	2.07	1.61	0.56	0.77	1.38	1.38	-	1.15
3.0	3.22	2.07	1.12	1.55	1.65	1.79	0.46	1.53
4.0	4.15	2.99	1.72	1.90	2.76	3.00	0.61	2.17
5.0	5.07	4.14	2.07	2.35	3.45	3.68	1.23	2.30
6.0	5.99	4.84	2.53	-	-	4.84	1.52	2.76
7.0	7.14	6.91	2.76	3.07	5.76	6.68	2.09	3.63
10.0	10.82	8.06	3.00	3.92	6.47	7.83	2.60	5.99

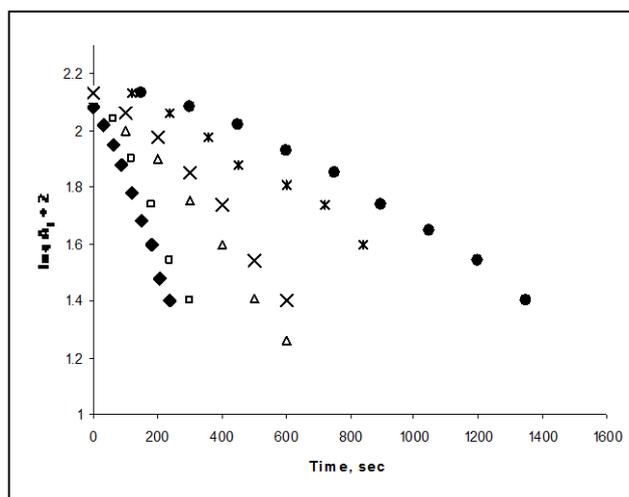


Fig. 2: Plot of  $\log [A]$  vs. time for the reduction of substituted aromatic nitro compounds in the presence of NaBH<sub>4</sub>. [Substituted nitro compound] =  $1 \times 10^{-4}$  mol dm<sup>-3</sup> [NaBH<sub>4</sub>] =  $5 \times 10^{-3}$  mol dm<sup>-3</sup> and [Ag catalyst] =  $0.5 \times 10^{-5}$  mol dm<sup>-3</sup>.

#### 4. Conclusion:

PEG core dendrimer encapsulated AgNPs synthesized through normal chemical reduction method were employed successfully for catalysing the NaBH<sub>4</sub> assisted reduction of substituted aromatic nitro compounds. The catalytic activity of dendrimer encapsulated AgNPs at different concentration of NaBH<sub>4</sub> was studied. Kinetic data of the pseudo first order catalytic reduction has been computed and reported. The synthesised dendrimer encapsulated AgNPs were found to be an efficient and cost

effective catalyst towards the reduction of substituted aromatic nitro compounds. The results of the study indicate that this could be adopted as a method for reducing similar type of compounds to eliminate them from the environment thereby restoring environmental green.

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