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Synthesis of Ibuprofen Intermediate using Alcoholic Silver Nanoparticles and its Kinetics: A Greener Approach towards Drug Synthesis

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ABSTRACT:

Silver nanoparticles (AgNPs) were prepared and tested for the activity in the catalytic reduction of 4-nitrophenol to 4-aminophenol showing to be exceptionally active. Further, using AgNPs we catalytically synthesized 1-(4-isobutylphenyl)ethanol which is important drug intermediate for the widely used Ibuprofen. The rate constants were determined at temperatures 298K, 303K, 308K, 313K, 318K, 232K correspond to 0.29 min^{-1}, 0.37 min^{-1}, 0.40 min^{-1}, 0.43 min^{-1}, 0.50 min^{-1}, 0.68 min^{-1}, respectively. The activation energy of AgNPs is 23.25 KJ/mol. The number of collisions of reactants in the term of frequency factor was found to be high 1.99×10^{8} $min.^{-1}$ and average heat of reaction is 26.1 KJ/mol. The recyclability study of AgNPs in the reduction of 1-(4-isobutylphenyl)ethanone (4-IBPEON) to 1-(4-isobutylphenyl)ethanol (4-IBPE) in six consecutive reaction cycles found to be (0.91g, 90 %), (0.89g, 88%), (0.87g, 86%), (0.84g, 83%), (0.84g, 83%), (0.81g, 80%), respectively. We promisingly minimize the waste generated in the synthesis of 4-IBPE by calculation E-factor and atom efficiency and was found to 0.57 and 81.56%, respectively. Reported experimental results were directly relevance to develop theoretical concepts.

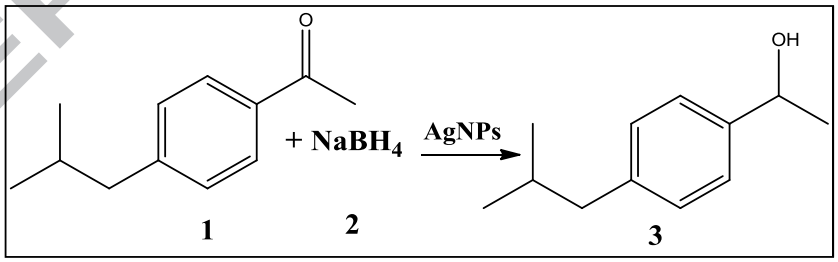
Keywords: Silver Nanoparticles; Catalytic Activity; E-factor; Recyclability; Ibuprofen; 1-(4-isobutylphenyl)ethanol.

1. Introduction

In the era of nanoscience and nanotechnology,[1] nanostructured material have played an important role in the catalytic synthesis of pharmaceutical drugs due to their high surface area, small particle size as well as "*nano-effect*"[2] originating from small size. Currently, a need to develop nanostructured materials based reduction methods for the synthesis of pharmaceutical drugs on industrial process is highly essential in order to minimize waste, and improve E-factors and atom efficiency.[3] This trend toward the green chemistry, to set high yield of product and environmentally benign processes that ascribes the economic value to eliminating waste. Noble metal nanoparticles (NPs) is of fundamental importance to the pharmaceutical, chemical, dyes and pesticides industries.[4,5] Amongst the NPs, silver nanoparticles (AgNPs) increasing interest towards the better catalytic performance because of cheap and attractive physiochemical properties. AgNPs, amongst other applications, has also been presently exploited as a catalyst in heterogeneous catalysis reactions.[6] For the synthesis of AgNPs variety of methods have been reported including chemical reduction method in aqueous solutions[7] or non-aqueous solutions,[8] template method,[9] electrochemical or sonochemical reduction method,[10] photocatalytic or photoinduced reduction method,[11] microwave assisted synthesis,[12] irradiation reduction method,[13] microemulsion method[14] biochemical reduction method[15] and many more. Foremost chemical reduction method in aqueous solution is the most conventional, clean and safe method. The uncapped AgNPs were commonly synthesized by chemical reduction method.[16] AgNPs have been widely used as catalyst in the model reaction of reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) by using $NaBH_4$.[17] The catalytic reduction of 4-NP was monitored by UV-Vis spectrophotometer under the mild reaction condition in aqueous medium.

Further, 1-(4-isobutylphenyl)ethanol (4-IBPE) is the most important drug intermediate for the synthesis of ibuprofen, a well-known non-steroidal anti-inflammatory drug (NSAID). We efficiently overcome, the use of hazardous organic solvents[18] reported so far in the synthesis of 4-IBPE from 1-(4-isobutylphenyl)ethanone (4-IBPEON) using aqueous ethanol which resulted in high yield of product. The E-factor (Environmental Factor) and atom efficiency (atom Utilization) are most important phenomenon towards greener and environmental benign synthesis.[19-21] The E-Factor is the most important concept played a major role in chemical industry, particularly in pharmaceutical industry, on the problem on waste generation in chemical manufacture. E-Factor is defined as the mass ratio of waste to desired product and the atom efficiency. Atom efficiency is the ratio of the molecular weight of the desired product to the sum of the molecular weights of all materials produced in the process.[19-21]

In present investigation we have reported for the first time the conventional catalytic synthesis of 4-IBPE from 4-IBPEON by using sodium borohydride ($NaBH_4$) in the presence of AgNPs in aqueous ethanol (Scheme – I).



Scheme 1. Synthesis of 4-IBPE from 4-IBPEON in the presence of AgNPs

The reaction was achieved successfully in six consecutive cycles of catalyst and completed within 5 – 10 minutes with high yield of product. Also, we have been promisingly reported the kinetics of AgNPs which are helpful to material chemistry researchers.

2. Experimental

2.1. Chemicals

All chemicals (4-nitrophenol ($C_6H_5NO_3$, 99%), sodium borohydride ($NaBH_4$, 99%), silver nitrate, ($AgNO_3$, 99.9%) 1-(4-isobutylphenyl)ethanone ($C_{12}H_{16}O$, 98%) and deionized water from Milli-Q system) were purchased from Sigma-Aldrich or Spectrochem or HiMedia and used as received.

2.2. Characterizations

The characterizations of AgNPs were collected from various instrumental techniques. The UV-Visible absorption measurement was performed on Shimadzu UV1800 Spectrophotometer. Water as blank and reference. Transmission electron microscopy was performed on a Philips CM-200 TEM operating at 200 kV, by depositing 20 µL of dispersed sample onto a 300 mesh copper grid coated with carbon layer IR spectra were collected at room temperature from Shimadzu FTIR-Affinity-1instrument in dried KBr pellets in the range 4000 to 400 cm^{-1}. The ^{1}H NMR spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz were collected from BRUKER AVANCE II Spectrometer using DMSO-d_6 as solvent and tetramethylsilane ($SiMe_4$) as internal standard. Mass spectra (MS) of 1-(4-isobutylphenyl)ethanol was collected from WATERS, Q-TOF MICROMASS (LC-MS) instrument.

2.3. Synthesis of Silver Nanoparticles (AgNPs)

The AgNPs were synthesized by using chemical reduction method. In brief, 10 mL of 1×10^{-3} M $AgNO_3$ taken in 50 ml of beaker and kept on magnetic stirrer. Then freshly prepared ice cold 30 mL solution of 2×10^{-3} M $NaBH_4$ was hastily added into $AgNO_3$ with vigorous stirring in which the colour change from black to orange and finally pale yellow was

observed. Then AgNPs solution was stirred for six hours for good stability and prepared nano-size of AgNPs particles. Finally, prepared AgNPs were kept overnight to remove excess hydrogen and used as a catalyst in the model after their characterization.

2.4. Typical Procedure for Catalytic Reduction of 4-nitrophenol (4-NP)

The heterogeneous catalytic reduction of 4-NP was performed at room temperature in air. In this typical reaction 1.0 mL of 5×10^{-2} M $NaBH_4$ and 10 µL of AgNPs were mixed for two minutes in 3.0 mL quartz cuvette. To this mixture 1.5 mL of 1×10^{-4} M PNP was added and mixed. The reaction was followed by observing the absorbance spectrum of 4-NP at λ 400 nm. The 4-NP spectrum diminished at every one minute time interval and new spectrum was observed at λ 300 nm is indicates that formation of new product, which was confirmed by isosbestic points.[22] This results were in good agreements with reported literatures.[23] The absorbance spectra were recorded within the wavelength range of 250 – 600 nm. Further, the same experiment were also performed in the temperature range of 298 – 323 K to determine the effect of temperature on the Pseudo first-order rate constant.

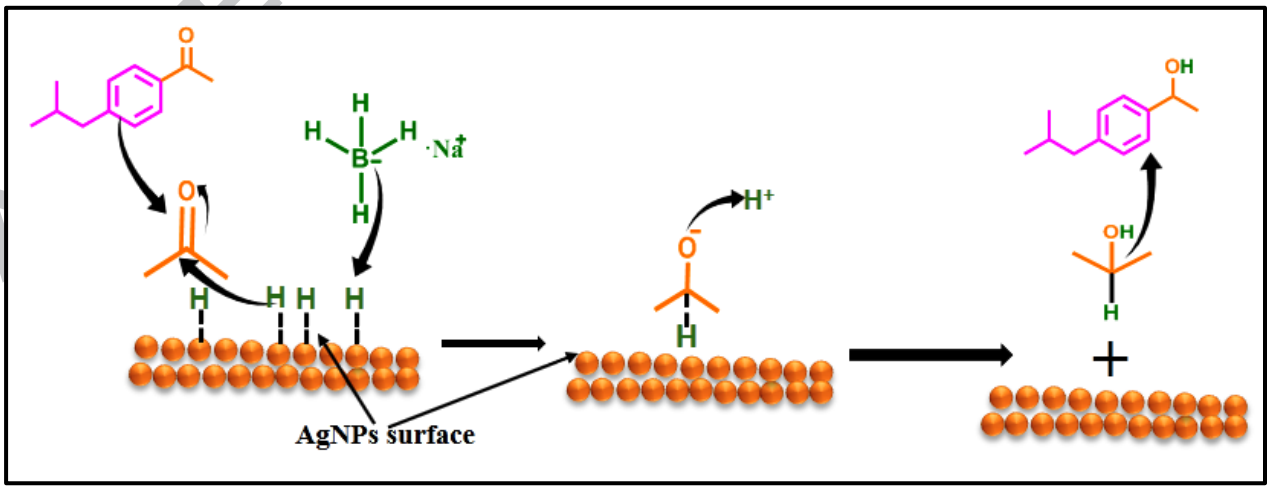
2.5. Synthesis of 1-(4-isobutylphenyl)ethanol (4-IBPE)

Aqueous ethanol (4.0 mL) was added in 3.0 mL of AgNPs in round bottom flask, kept in ice bath with constant stirring. This mixture we named as "*Alcoholic AgNPs*". In the mixture 0.43 g of $NaBH_4$ was slowly added and finally 1.0 g. of 4-IBPEON added with constant stirring. After complete addition, the reaction mixture was removed from the ice bath and stirring was continued at room temperature. The reaction was completed within 5 to 10 minutes and it was preliminary confirmed by thin layer chromatography (TLC). The product was isolated using ethyl acetate as organic layer and AgNPs remained in alcoholic layer. The solvent was removed by rotary evaporator and product was dried at room temperature.

2.6. Recycling Studies

The recycling study of AgNPs were reported so far, for the catalytic reduction of 4-NP to 4-AP. The above (4-NP to 4-AP) recycling confines towards, used concentration of reactant was low, the reaction was monitor by UV-Vis spectrophotometer. For the first time we have performed the recycling study of AgNPs in the reduction of 4-IBPEON to 4-IBPE. In detail, as discussed above (**2.5**), we synthesized 4-IBPE in first cycle. In second cycle in alcoholic liquor containing AgNPs was added 1.0 g of IBPEON and 0.43 g of $NaBH_4$ with constant stirring at room temperature. After completion of reaction, the product was isolated from ethyl acetate as organic layer and AgNPs remained in alcoholic layer. Finally the solvent from the product was removed by rotary evaporator. Repeated the similar procedure for next consecutive reaction cycles and recorded the percent yield of product in every cycles. We conclude that the AgNPs showed good catalytic activity against poisoning of catalyst after six consecutive reaction cycles.

2.7. Reaction Mechanism



Scheme 1 reaction mechanism: Reduction of 4-IBPEON to 4-IBPE in the presence of AgNPs.

In the mechanism of reduction reaction of 4-IBPEON to 4-IBPE involves the initial adsorption of 4-IBPEON and BH_4^- ions on the catalyst surface. Due to the close vicinity of the reacting groups on the catalyst surface, the reduction becomes practicable. The catalyst provide surface and helps this reduction process by relaying hydride ion to from BH_4^- ions to the 4-IBPEON to forms 1-(4-isobutylphenyl)ethanoate ion. This ion absorbs proton solvent and finally forms 4-IBPE.

3. Results and Discussion

3.1. UV-Vis. Spectrometry of Silver Nanoparticles (AgNPs)

The synthesized AgNPs by chemical reduction method were confirmed by UV-Vis Spectrophotometer that showed the narrow surface plasmon resonance (SPR) band at 405 nm. **(Figure 1).** Two different SPR were observed for AgNPs, and alcoholic AgNPs. The black SPR was recorded before proceeding the reaction while blue SPR was recorded after completion of all reaction cycles (after cycle 6). The broad peaks showed in inset of figure 1. After completion of every reaction cycle UV-Vis spectra was recorded. We observed that decrease in SPR of alcoholic AgNPs was due to the dilution of AgNPs by addition of reactants in every reaction cycle.

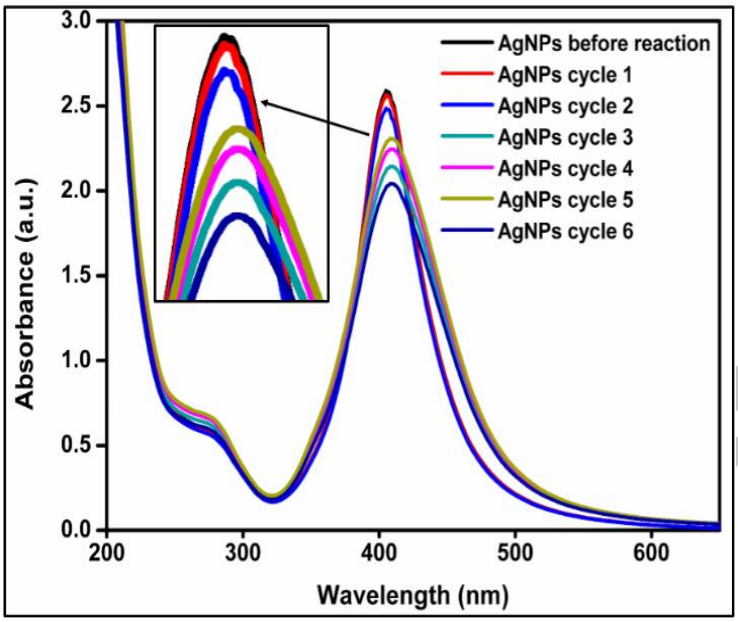


Figure 1. UV. Vis SPR of AgNPs, black SPR before reaction and blue SPR (cycle 6) after reaction.

3.2. Morphology of silver nanoparticles (AgNPs)

The morphological study using TEM of synthesized AgNPs was carried out **(Figure 2, panel a, b).** It was observed that the spherical shaped rigid particles having a narrow size distribution showed good catalytic activity and high surface area. The particles were uniform and distinctly present in aqueous collide solution. There was no change found in morphology of AgNPs by adding alcohol **(Figure 2, panel c).** It proved that the TEM image of alcoholic AgNPs is in agreements with AgNPs and thus, it confirmed that the AgNPs showed good stability after six consecutive reaction cycles. The average particle size of AgNPs (12 ± 0.84 nm) **(Figure 2. Panel d)** was confirmed by TEM image.

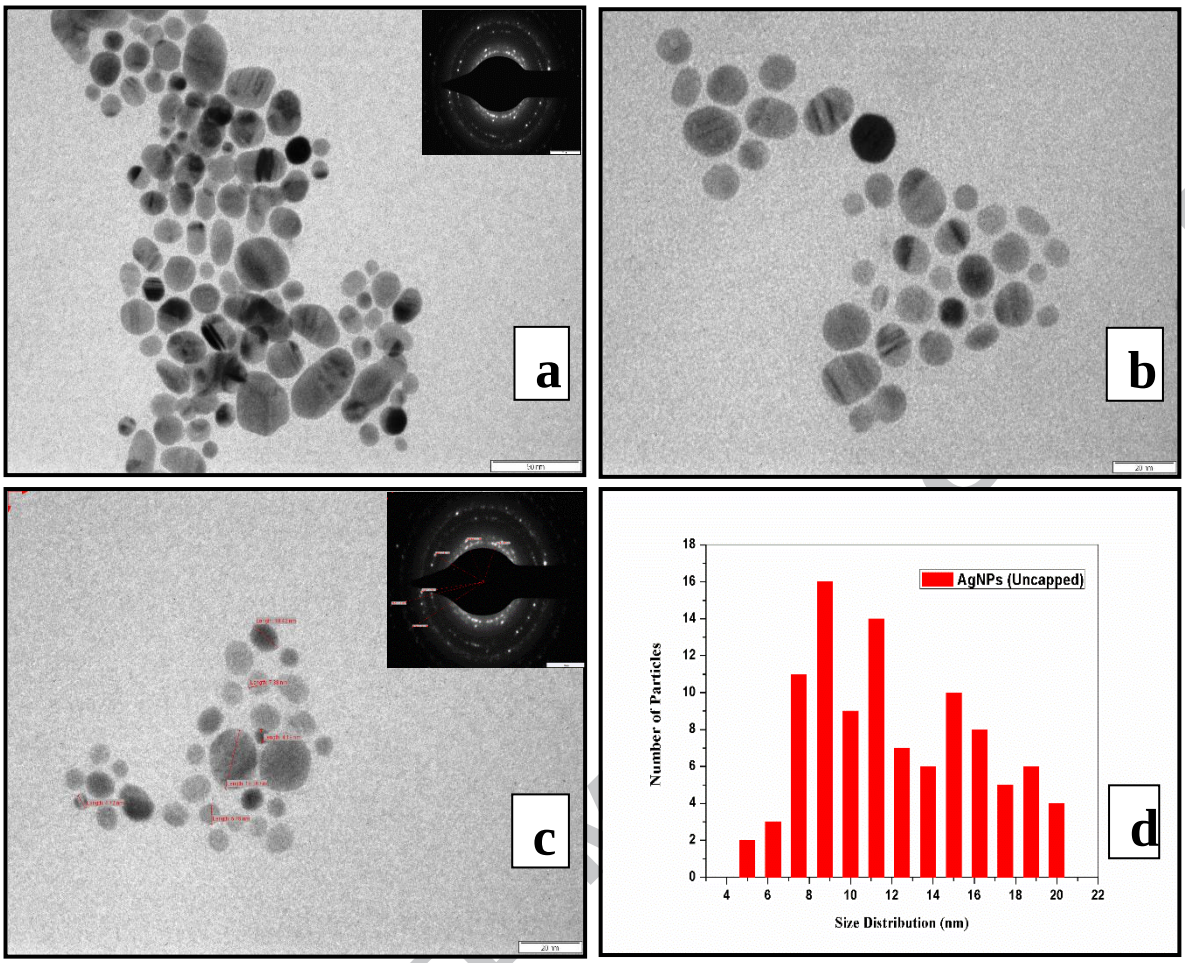


Figure 2. TEM image of AgNPs (panel a, b) and alcoholic AgNPs (panel c); panel a) and c), inset is the selected area electron diffraction (SAED) pattern. d) Particle size of AgNPs showing average size is about 12 ± 0.84 nm approx.

3.3. Kinetics and catalytic activity of silver nanoparticles (AgNPs)

The kinetics study was performed by using Langmuir-Hinshelwood mechanism.[22] Assuming that 4-NP and $NaBH_4$ adsorbed on the surface of AgNPs, the interaction of $NaBH_4$ on the surface of AgNPs took place and which ultimately led to the liberation of hydrogen and 4-NP was converted to 4-AP. In general, the rate law for 4-NP reduction by $NaBH_4$ is given by Equation(1),

$$-\frac{d[4NP]}{dt} = k[4NP]^a\,[BH_4^-]^b \qquad (1)$$

In the Eq. (1) k is the pseudo-first order rate constant, calculated from Langmuir-Hinshelwood equation given by equation (2).

$$\ln \frac{C_0}{C} = kt \quad (2)$$

In the Eq. (2), C_0 and C are the initial and final concentrations having equivalent in terms of (A_0 and A_t respectively) monitor at fixed wavelength at time t, k is the pseudo-first order rate constant for AgNPs. Hence, for the constant catalyst concentration, a plot of $\ln(A_0/At)$ with respect to time gives straight line whose slope is the k. The k also determined at various temperatures ranging from 298 – 323 K and activation energy (Ea) of the catalytic reduction of 4-NP to 4-AP by using AgNPs was calculated by Equation (3).

$$k = A\, e^{-Ea/RT} \quad (3)$$

In the Equation (3), k is the pseudo-first order rate constant at temperature T, A is the frequency factor, Ea is the activation energy, R is the universal gas constant (8.314 $JK^{-1}mol^{-1}$) In the catalytic reduction of 4-NP to 4-AP by using $NaBH_4$ in the presence of AgNPs the heat of reaction ΔH for the solution phase reaction is calculated from the Equation (4).

$$\Delta H = Ea + RT \quad (4)$$

In order to study the effect of temperature on the pseudo-first order rate constant, **(figure 3.)** the reactions were also performed in the temperature range of 298 K to 323 K. The temperature of the solution in the quartz cuvette was controlled by water circulated peltier unit with an accuracy of temperature ± 0.3^0C inside the cuvette holder.

Figure 3. (Panel a, b, c, d, e, and f) Illustrate that as the temperature increases in the range of 298K to 323K for the reduction of 4-NP rate of the reaction also increased. *i.e.* temperature is directly proportional to rate of reaction. At the temperature 298 K, 4-NP reduced within 13 minutes for the AgNPs catalyzed reaction at 400 nm. Similarly for different temperatures 303 K, 308 K, 313 K, 318 K and 323 K, reduced in 10, 7, 8, 8 and 5 minutes, respectively. Finally, we conclude that pseudo-first order kinetics was observed at all temperatures and delay of time is reduced with increasing temperature.[24-26] **(See ESI Figure S1, a)** The pseudo-first order rate constants were determined by plotting ln(Ao/At) as a function of time.

(Figure 3, insets a, b, c, d, e and f). To know the heterogeneous catalytic mechanism of AgNPs in the reduction of 4-NP to 4-AP, the pseudo-first order rate constants were also determined at temperature ranging from 298K to 323K. The calculated rate constants with respect to temperatures 298K, 303 K, 308K, 313K, 318K and 323K were found to be 0.29 S^{-1}, 0.37 S^{-1}, 0.40 S^{-1}, 0.43 S^{-1}, 0.5 S^{-1} and 0.68 S^{-1}, respectively. From this investigation the rate constants were increased as temperature increased and also strictly follows pseudo-first order kinetics **(Table 1.).**

Activation energy of metal nanostructures likely depends on the size and shape of nanoparticles.[27] For the determination of activation energy of the reaction, temperature dependent study were performed from 298K to 323K for AgNPs catalyzed reduction of PNP to PAP **(see ESI, figure S1, a)** and the pseudo-first order rate constants for AgNPs were fitted using Arrhenius equation **(Equation 3)** and the activation energy was calculated using the slope of the linear plot of ln (k) versus 1000/T **(see ESI, Figure S1 panel b).** The calculated activation energy for AgNPs was found to be 23.58 KJ/mol. The activation energy calculated for the AgNPs catalyzed conversion of 4-NP to 4-AP in this study is lowest so far, while the

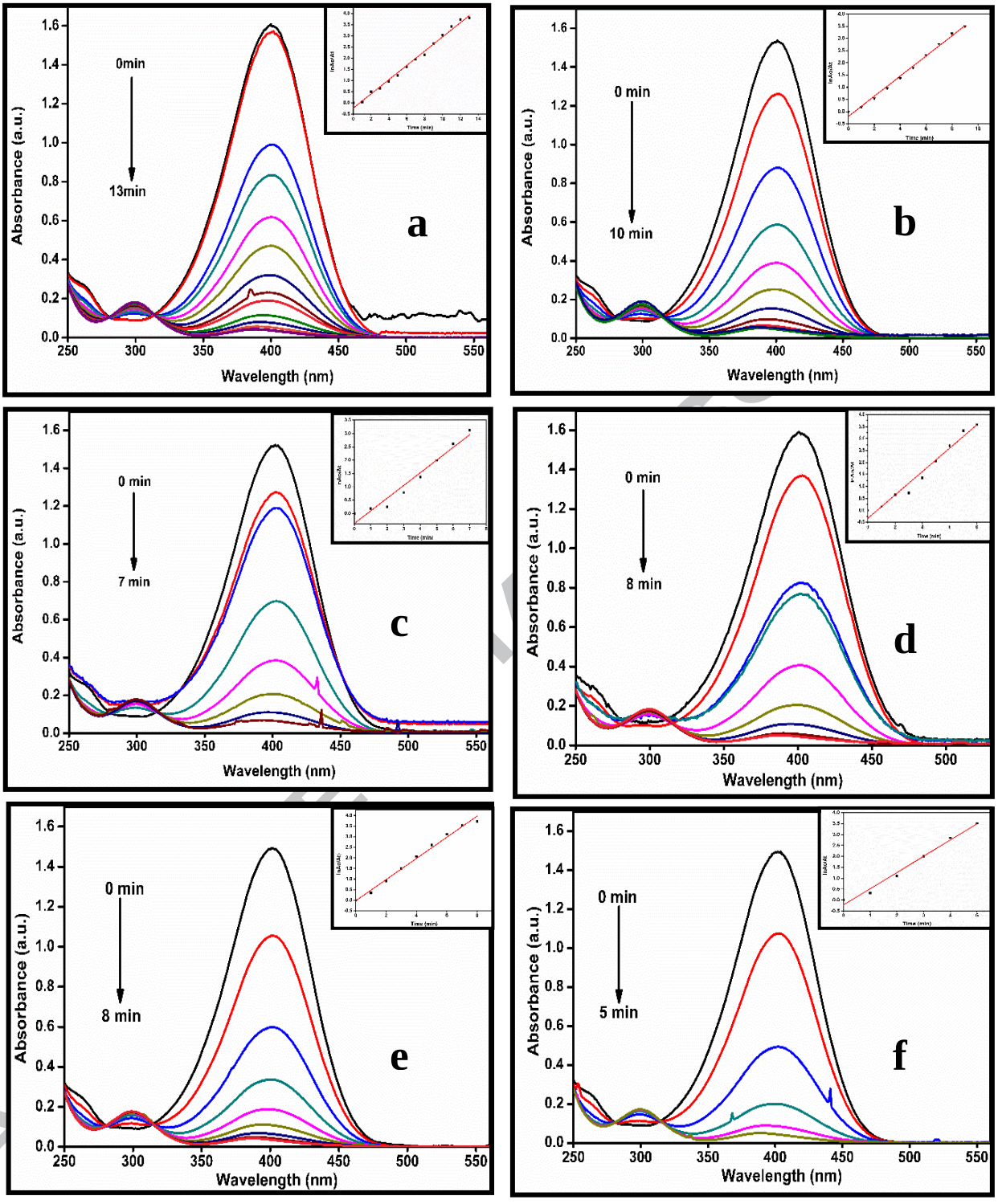


Figure 3. The UV-Vis plots of absorbance as a function of wavelength at temperature a 298K; b 303K; c 308K; d 313K; e 318K; f 323K for regular time intervals indicates the disappearance of peak of 4-NP due to the catalytic reduction of 4-NP to 4-AP by using NaBH4 in presence of AgNPs; in inset of each panel shows corresponding linear plots of ln (Ao/At) versus time. Reaction conditions: [4-NP] = 1×10^{-4} M; [NaBH4] = 5×10^{-2} M; [AgNPs] = 2.5×10^{-4} M.

lowest activation energies 33.8 – 45 KJ/mol has been reported for AgNPs and AgNPs supported different agents or composites.[27-30] From the Arrhenius equation frequency factor was determined and found to very high.1.99 × 10^8 per min. **(Equation 3)** Higher the frequency factor proved more number of collisions of reactants. The average heat of reaction for the reduction of 4-NP to 4-AP was found to 26.1 KJ/mol. **(Equation 4)**. E-factor and Atom efficiency (atom utilization) are the most important concept for metal catalyzed reactions towards the environmental benign synthesis. In the present investigation the concept E-factor and atom efficiency were studied for AgNPs catalyzed reduction of 4-IBPEON to 4-IBPE **(Scheme-1).** E-factor was found to 0.57 and proved that very minimum of waste was generated in the synthesis of 4-IBPE. Also, the atom efficiency was found to 81.56% and proved that higher number of atom involved in the formation of product 4-IBPE.

Table 1. The rate constants (k), at different temperatures, the activation energy (Ea), frequency factor (A) and average heat of reaction for AgNPs catalyzed reduction of 4-NP to 4-AP by using $NaBH_4$

	Temperature T/(K)	Rate Constant k/min^{-1}	Activation energy (Ea)/KJ/mol	Frequency factor A/min	Average Heat of reaction ΔH/KJ/mol
AgNPs	298	0.29 ± 0.04	23.58	1.99 × 10^8	26.1
	303	0.37 ± 0.03			
	308	0.40 ± 0.01			
	313	0.43 ± 0.01			
	318	0.50 ± 0.01			
	323	0.68 ± 0.03			

Table 1, shows the kinetic evaluation of AgNPs, the rate constant was found to be steadily increasing with temperature. At temperature 298K, 4-NP reduced in 13 minutes while at 323K 4-NP reduced within 5 minutes, is also proves that the AgNPs were stable at temperature 323K and reduced fastly due to the rigidity of nanoparticles reported in TEM

images. The activation energy (23.58 KJ/mol) was also lowered and frequency factor was found to be very highest (1.99×10^8), which concluded that higher the collisions of reactants in solution on the surface of AgNPs due to small particle size of AgNPs provide high surface area and finally lower the activation energy and increase the rate constant with respective to temperature. Finally, the heat of reaction at different temperatures was calculated and the average of heat of reaction was found to be 26.1 KJ/mol.

In the comparative study of AgNPs **(Table 2)**, we found the lowest activation energy with high frequency factor and lower heat of reaction because of high catalytic activity of AgNPs.

Table 2. The comparison of AgNPs with different stabilizing agent or supporting agents, size, rate constant, activation energy, frequency factor and heat of reaction

Nanoparticles	Size of Nanostructures/nm	Rate Constant k/min^{-1}	Activation energy (Ea)/KJ/mol	Frequency factor A/min	Heat of reaction ΔH/KJ/mol
AgGME[30]	25	ND	41.00	ND	ND
AgDENs[31]	3.37 ± 0.6	0.0001	45.7	ND	34 ± 2.7
AgNPs[32]	ND	ND	35.16	ND	ND
AgNPs[#]	**7 - 13**	**0.37**	**23.58**	**1.99×10^8**	**26.1**

*ND = Not Determined. # = In this work.

3.4. Yield and Characterization of 1-(4-isobutylphenyl)ethanol (4-IBPE)

We have been demonstrated catalytic reduction of 4-IBPEON to 4-IBPE by using $NaBH_4$ in the presence of AgNPs dispersed in dilute alcohol in the interest of well-known model reaction for the catalytic reduction of 4-NP to 4-AP. The stability of catalyst have been studied by recycling and found to be stable to six successive cycles in laboratory scale. The

reaction was practically conducted on laboratory scale in the laboratory by with 1.0 gm of 4-IBPEON and 3 mL of AgNPs and preliminary monitored by thin layer chromatography (TLC) and melting point. As shown in figure 4. The yield of the 4-IBPE was slightly decreased with respect to recycling cycles and found to be (0.91g, 90 %), (0.89g, 88%), (0.87g, 86%), (0.84g, 83%), (0.84g, 83%) and (0.81g, 80%) with respect to cycles 1 to 6, respectively (Figure 4).

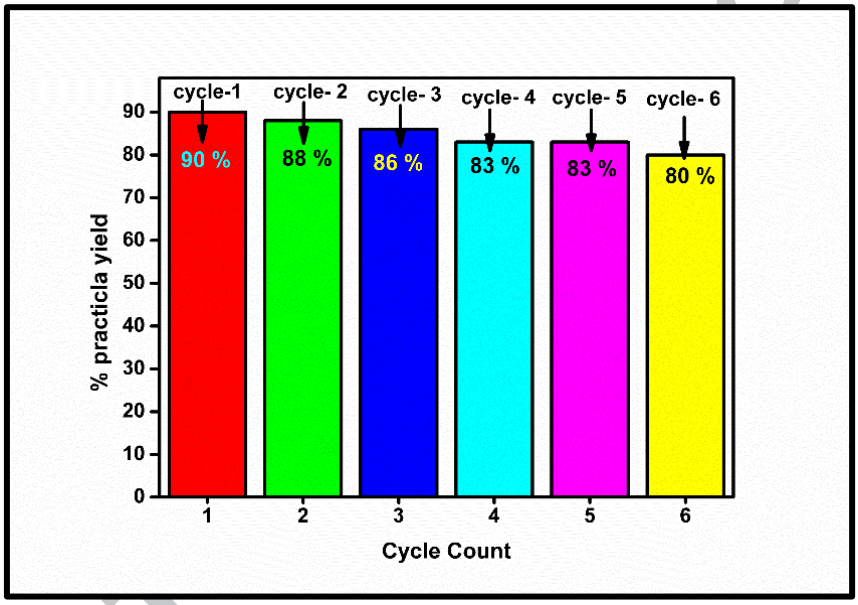


Figure 4. Percent practical yield of 4-IBPE against number of cycle count.

Lastly, the synthesized 4-IBPE was characterized by using FTIR, ^{1}H NMR, ^{13}CMR and mass spectroscopy (For spectra see SI, Figure S2, S3, S4 and S5). The characterization data of 4IBPE as given below.

Spectral data of 3. 1-(4isobutyl)phenyl ethanol (IBPE) is isolated as viscous oil; b.p. 245-246 ^{0}C; FT-IR (KBr) cm^{-1}: 3336 (OH), 2954-2899 (CH); 1666-1624 (C-C=C), ^{1}H NMR (400 MHz, $CDCl_3$,) δ_H: 0.88 (6H, d, J = 6.6 Hz); 1.40 (3H, d, J = 6.4 Hz), 1.83 (1H, m, CH), 2.43 (2H, d, J = 7.1 Hz CH_2), 2.71 (1H, br s, OH), 4.76 (1H, q, J = 6.4 Hz CH), 7.07 (2H, d, J = 8.08 Hz, Ar-H), 7.21 (2H, d, J = 8 Hz, Ar-H), ^{13}C NMR (400 MHz, $CDCl_3$,) δc: 22.5 , 25.1, 30.3, 45.2, 70.0, 125.3, 129.1, 140.7, 143.3; ESI-MS: m/z = 177.13 $[M - H]^{+}$, 161.09 [M-OH]

The result were found to be well agreement with the reported literatures to conform the product 4-IBPE.

4. Conclusion

In summary, we have efficiently investigated the catalytic performance of AgNPs in the reduction of 4-NP to 4-AP by using $NaBH_4$. In the UV- Vis spectra observed isosbestic points, recyclability of catalyst and kinetics all have to be accounted by keeping an eye on to the published mechanism. The recyclability study of AgNPs has been reported for the first time and investigated in the reduction of 4-IBPEON – 4-IBPE by using $NaBH_4$ in "*Alcoholic AgNPs"* and found to be in the range of very excellent to good with better yield of 4-IBPE in each stage of total six cycles. This work useful to study the stability of AgNPs which are withstand in the organic reaction conditions to improve the catalytic recycling and efficiency for many applications. We also successfully determined E-factor and atom efficiency, were proved minimization of waste generated. The costly and important drug intermediate of Ibuprofen, 4IBPE was economically synthesized in the laboratory by environmentally benign process. In future, attempts will made to scale up the synthesis of 4-IBPE in pilot plant by collaboration with pharmaceutical industry. This results of the present investigation could be helpful for material chemistry scientists as well as organic researches to design the safer synthesis of important commonly used pharmaceutical drugs.

5. Acknowledgements

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6. Supplementary Information (SI)

In the additional information containing temperature dependent catalytic reduction of 4-NP by UV-Vis. Spectroscopy with corresponding Arrhenius plot (figure S1) and spectral data containing IR spectra (Figure S2), ^{1}H and ^{13}C NMR (Figure S3, S4) and mass spectra (Figure S5) are given in supporting information.

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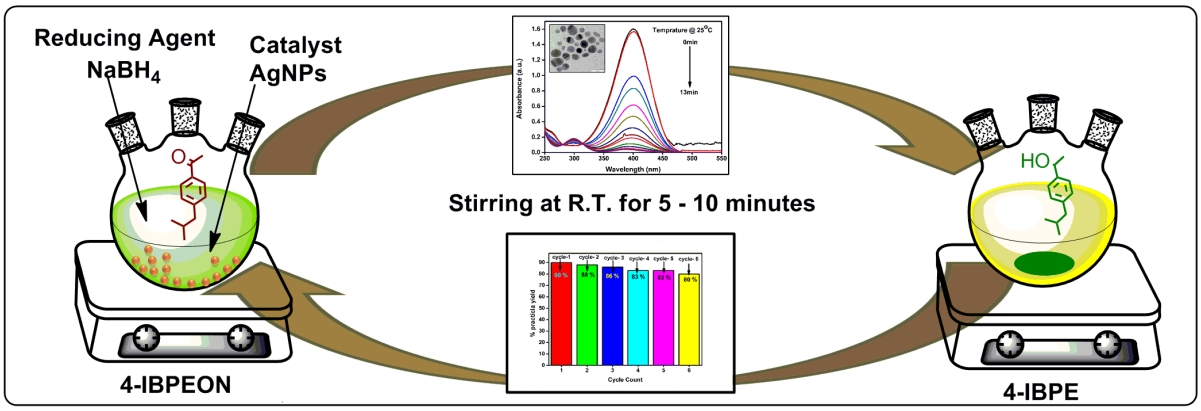
Graphical abstract



Highlights

- Synthesised and kinetics of bare AgNPs, showed good catalytic activity in the model reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP).
- Environmentally benign synthesised 1-(4-isobutylphenyl)ethanol from 1-(4-isobutylphenyl)ethanone by using AgNPs as catalyst.
- Six times recycled AgNPs as a catalyst in the synthesis of of 1-(4-isobutylphenyl)ethanol with high yield.
- E-factor and atom efficiency were calculated to evaluated waste generated in the process.