Preparation of Ni nanocatalyst for improved hydrogenation of nitro-aromatics

A thesis

Submitted in the partial fulfillment of the requirements for the award of degree of

MASTER OF SCIENCE
in
CHEMISTRY

Submitted by

Himanshi
(Roll No. 301702014)

Under the supervision of

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June, 2019

Certificate

I hereby certify that the work presented in this thesis entitled "**Preparation of Ni nanocatalyst for improved hydrogenation of nitro-aromatics"** submitted in partial fulfillment of the requirements for the award of degree of Master of Science in Chemistry submitted to School of Chemistry and Biochemistry, Thapar Institute of Engineering and Technology, Patiala is an authentic record of my own work carried out under the supervision of Dr. Bonamali Pal.The work has not been submitted to any other University for the award of any other degree or diploma.

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This is to certify that the above statement made by the candidate is correct and true to the best of my knowledge.

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Above all I am thankful to my parents for their blessings, support and encouragement.

Date:

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Abstract

The work describes the synthesis of two different shape Ni nanoparticles for the improved catalytic hydrogenation of nitro-aromatics. These Ni NPs were analyzed using different characterization techniques i.e. X-ray diffraction (XRD), UV-vis spectra, Diffused light scattering (DLS), scanning electron microscopy (SEM) & Transmission electron microscopy (TEM). The morphology studies revealed that Ni-NP1 was found to be irregular nanospheres and Ni-NP2 as agglomerated nanowires. From the XRD analysis the crystallize size for the Ni-NP1 and Ni-NP2 found to be 8 nm and 14 nm respectively. These Ni-NPs was analyzed for the catalytic hydrogenation of p-nitro phenol. It was observed that Ni nanospheres (NP1) shows higher %yield (89%) for the catalytic hydrogenation of nitro-aromatics compared to Ni nanowires (NP2) & commercially available Raney Ni. The kinetic measurement shows that the hydrogenation of nitro-aromatics follows pseudo first order and Ni NP1 exhibited higher rate constant of 1.5×10^{-2} min^{-1} compared to NP2 & Raney Ni. Hence, the synthesized nickel nanoparticles could be efficient and effective catalyst for the hydrogenation of industry important nitro-aromatics.

List of abbreviations

NP: Nanoparticles

EG: Ethylene glycol

RB: Round bottom

DLS: Dynamic light scattering

XRD: X-Ray Diffraction

SEM: Scanning electron microscopy

TEM: Transmission electron microscopy

FTIR: Fourier transformation infrared spectroscopy

HPLC: High performance liquid chromatography

PNP: p-nitrophenol

PAP: p-aminophenol

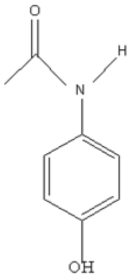
1. Introduction

Over past many years, Nano-science and Nano-technology has become an important field of research and development among the scientists. Nanoparticles are the microscopic particles with a size less than 100nm. They act as a bridge between bulk particles and the atomic structures. Due to their small size, shape and large surface to volume ratio, they exhibit various optical, magnetic, electric and catalytic properties. Currently, metal NPs have attracted much attention due to their catalytic and magnetic properties. More attention has been paid to transition metals nanoparticles like Ni, Fe and Co due to their magnetic property and applications[1]. It has been seen that the physical and chemical properties of these metal NPs are size and shape dependent. Amongst these metal NP, study of nickel nanoparticle has been of greater resource for research because of its high selectivity and high catalytic properties mainly in the hydrogenation reactions.[2] Therefore, various methods to synthesize the Ni NPs have been reported in the literature.

In chemical industries, catalytic reactions are carried out on large scale which consumes a great amount of energy and resources which produces lot of wastage. Raney Ni is an industrial metal catalyst used on large scale. Its easy availability makes it favorable for the industry to use in the catalytic reaction. But it has some disadvantages too. Raney Ni is pyrophoric when dry and hence kept in submerged water. Secondly, it must be separated from the reaction mixture. Thirdly, it contains small amount of alumina (Al_2O_3) which initiates some side reaction thus altering the results[3]. This supports synthesis of Ni nanoparticles for the catalytic reactions. Yang Du *et.al* (2004)[4] reported the inferior catalyst activity of Raney nickel in reduction of nitro compounds. Further Hiabin Jiang *et.al* (2016)[5] reported synthesis of polymer supported raney nickel but it only stopped the formation of simple organic byproducts. Hence metal based nanoparticles helped to overcome all these factors.

In recent years, nickel NP have been synthesized of various shapes like nanocubes, nanoflowers, nanorods etc. by various methods like chemical reduction, hydrothermal method and micro-emulsion method. Y.Sourmare e*t.al* reported in his paper about the synthesis of nickel nanowires by polyol method for studying the magnetic properties of nickel nanowires[6]. Therefore an alternative way to synthesize the nickel NP is by using polyol method which is also called soft chemical method. In this method a metal is suspended along with glycol solvent and refluxed; where EG acts as a reducing agent which prevented agglomeration of nanoparticles .It also helps to control the particle size and its reductive ability helps to reduce the metal into metal NP[7-8] .The synthesized nickel NP has its various applications in automotive catalyst convertor [9], hydrogenation reactions [10], super capacitors [11]etc.

Nitro-aromatic compounds are the organic compounds with nitro group attached to it. They act as a major group of chemicals used in the industry. It has various application in synthesis of dyes, polymers, pesticides and explosives.[12] Among these there are some nitro-aromatics which are hazardous to the environment. One of the compound is p-nitrophenol which is one of the industry pollutant whereas on reducing p-nitrophenol the product obtained is p-aminophenol which has its application in drug formation and one of the reactant in synthesis of drugs like paracetamol and phenacitin (Fig.1 & Fig.2).[13] It is also used in cosmetic industry for manufacturing of hairs and dyes.[14] S.M El.Sheikh1[15] *et.al* carried catalysis reaction of reduction of p-nitrophenol by mesoporous silica with gold and palladium metal based catalyst but the metals used were expensive. The reduction was carried forward by addition of $NaBH_4$ which was time consuming. In previous studies, hydrazine monoformate was also used for the catalytic reduction reported by G.Shankare *et.al* but it had disadvantage that it interacted with the nickel salt to form nickel formate[16]. Therefore, alternative use of hydrogen source was necessary for the catalytic reaction. We confirmed less literature has been found for the catalytic reaction initiated by hydrogen gas under pressure.



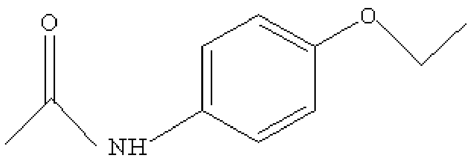


Fig.1 Paracetamol

Fig.2 Phenacitin

Hence, our aim has the following objectives:

1. Preparation and characterization of Ni nanoparticles of different morphology
2. To study its catalytic activity for the hydrogenation of p-nitrophenol to p-aminophenol

2. Materials and Methods

2.1 Materials

Nickel (II) chloride hexahydrate ($NiCl_2.6H_2O$), hydrazine hydrate ($N_2H_{4.}$ H_2O), distilled water, sodium hydroxide (NaOH) and ethylene glycol were all obtained from Loba chemicals.

2.2 Synthesis of Nickel Nanospheres (NP1)

All the reactants were dissolved in EG. In the experiment, 50ml of 15mM $NiCl_{2.}6H_2O$, 30 ml N_2H_4 and 1M NaOH solutions were mixed in the round bottom flask under magnetic stirring and condenser on top. First, hydrazine solution was heated to 184°C, then the mixture of Ni^{2+} salt was added as soon as the boiling point is reached. Optimum temperature of 184°C is maintained throughout the synthesis with the help of oil bath which is monitored by thermometer. Further, an appropriate amount of NaOH solution was prepared and added drop wise to the mixture until the mixture turns basic with pH 12. Soon the whole mixture turned blue and finally black indicating the formation of Ni metal. The mixture was heated for 3 hours under continuous stirring (Fig. 3). After the reaction got completed, the mixture was allowed to cool down at room temperature. The particles were then collected after centrifuging at 7000rpm and washed with ethanol and water for 5times. Now, the prepared Ni nanoparticles were dried in oven at 70° C overnight.[17] The stoichiometric equation can be expressed as follows:

$$2Ni^{2+} + N_2H_4 + 4OH^- \longrightarrow 2Ni + N_2 + 4H_2O$$

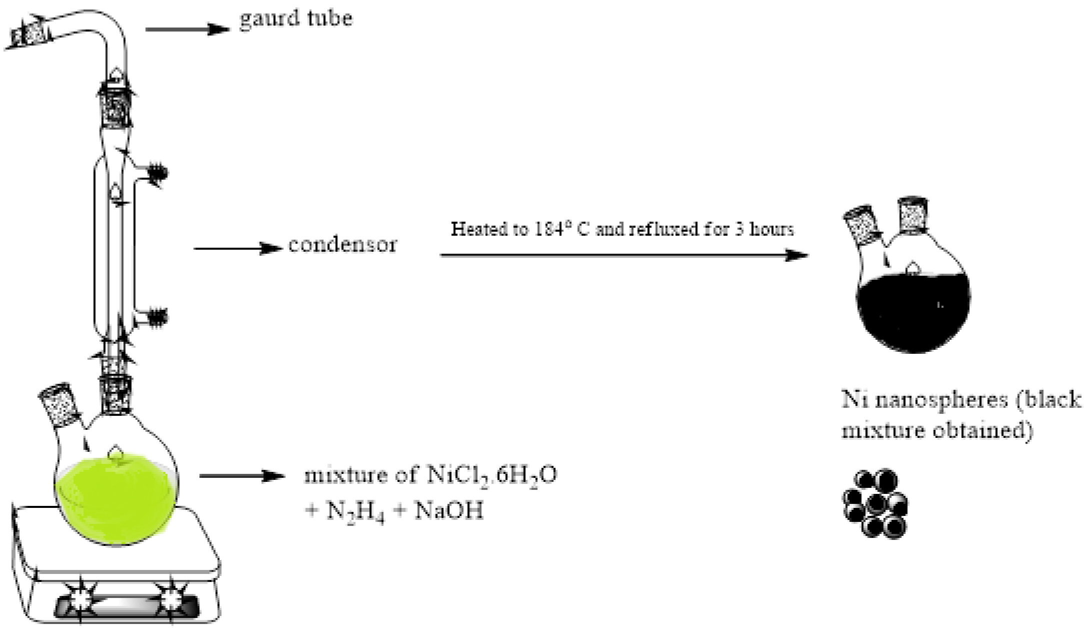


Fig. 3 Systematic diagram of synthesis of nickel nanospheres (NP1)

2.3 Synthesis of Nickel Nanowires (NP2)

1M of $NiCl_2.6H_2O$ in 7.5ml EG were mixed, heated to 120°C and refluxed. Then, 10ml hydrazine was added to it. 1M NaOH solution was prepared and added drop wise until the solution turned basic. The solution was heated for 2 hours until the solution turned black. The synthesized nanoparticles were then centrifuged at 7000rpm and washed with water for 3times. Washing with ethanol was also done to remove any other impurities. The obtained nanoparticles were then dried at 70°C in oven.[18] The proposed mechanism (Fig. 4) is given below:

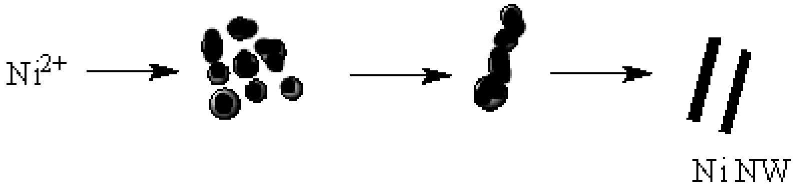


Fig.4 Proposed mechanism of synthesis of nickel nanowires (NP2)

2.4 Catalytic activity for the hydrogenation of p- nitro phenol

The catalytic activity of prepared nickel nanospheres and nanowires was checked by hydrogenation of p-nitro phenol. Further their activity was compared with commercial available Raney Ni. First, 20µL of 5mM solution of p-nitrophenol was taken in the RB flask. Then added the prepared Ni nanoparticles in different proportion and refluxed. The hydrogen balloon was attached to the top of the condenser through the connector. The reaction was carried out at 70°C throughout. Within 3 hours the yellowish – green solution of p-nitrophenol turned white which showed the completion of the reaction. This means p-nitrophenol has been reduced to p-aminophenol succesfully. Now this reaction with same reaction conditions was done with NP1, NP2 and Raney Ni by taking 3mg, 5mg, 7mg of the catalyst respectively and its catalytic activity was investigated**.** (Fig.5)

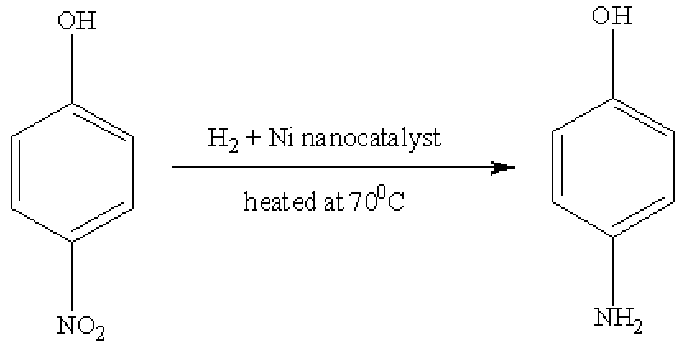


Fig. 5 Catalytic hydrogenation of p-nitrophenol to p-aminophenol with nickel NP1 & NP2 at 70°C

3. Characterization Techniques

To study the morphology and characteristics of synthesized nanoparticles and also to study the catalytic activity of nanoparticles various methods and techniques were used.

3.1 UV spectroscopy analysis was done to characterize the metallic nature of Ni nanoparticles over the wavelength range 200nm – 800nm.

3.2 Dynamic Light Scattering (DLS) technique was used to determine the particle size of the Nickel nanoparticles by Malvern ZEN3600 particle size analyzer.

3.3 X-ray diffraction studies were done to determine the crystallographic structure and crystalline size of nanoparticles. It was determined by PAN analytical- Xpert High score with a diffraction angle of 2θ.

3.4 High Performance Liquid Chromatography (HPLC) was performed to determine the retention time of the product obtained by reaction with nano catalyst.

3.5 TEM analysis was done to determine the different morphology and size of the nickel nanoparticles.

3.6 SEM analysis was done to determine the surface morphology of the nickel nanoparticles.

4. Results & Discussion

4.1. Optical studies and Structural analysis

UV-visible spectra

Fig. 6 shows the UV-visible spectra of the synthesized NP1 and NP2.The strong absorption band at 255nm was observed for NP1 and the absorption peak at 270nm was observed for the NP2. The shift in the maximum wavelength of the NP1 and NP2 is because of the different size and morphology.

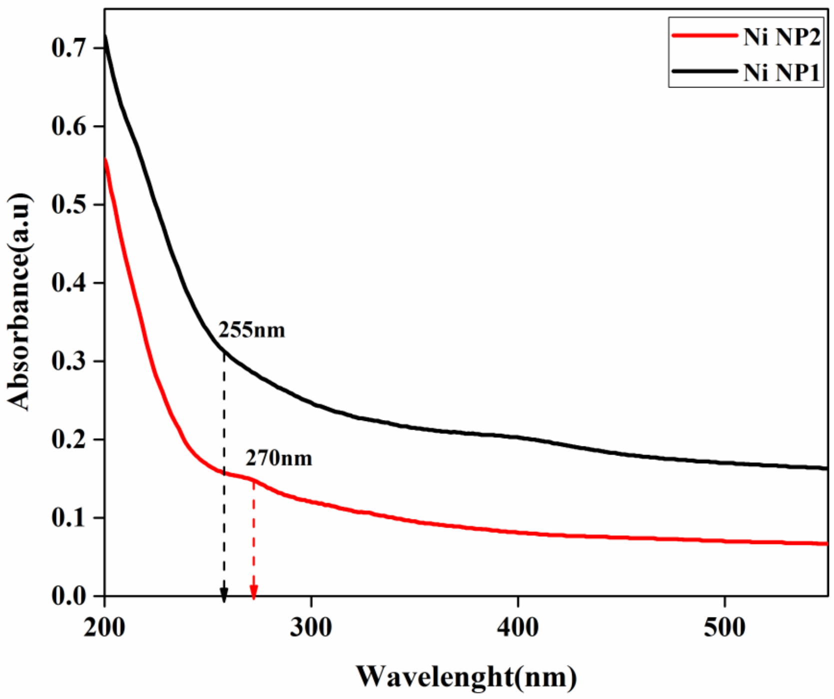


Fig.6 UV-visible spectra of synthesized Ni nanoparticles

DLS analysis

The particle size distribution of synthesized nanoparticles were obtained by using dynamic light scattering (DLS) technique. Fig. 7 shows an average hydrodynamic size of 97nm and 181nm for NP1 and NP2 respectively. Further the average particle size was compared with the commercially available Raney Ni which was found to be around 500nm. The small size of the nanoparticles is due to the solvent EG which prevents agglomeration.

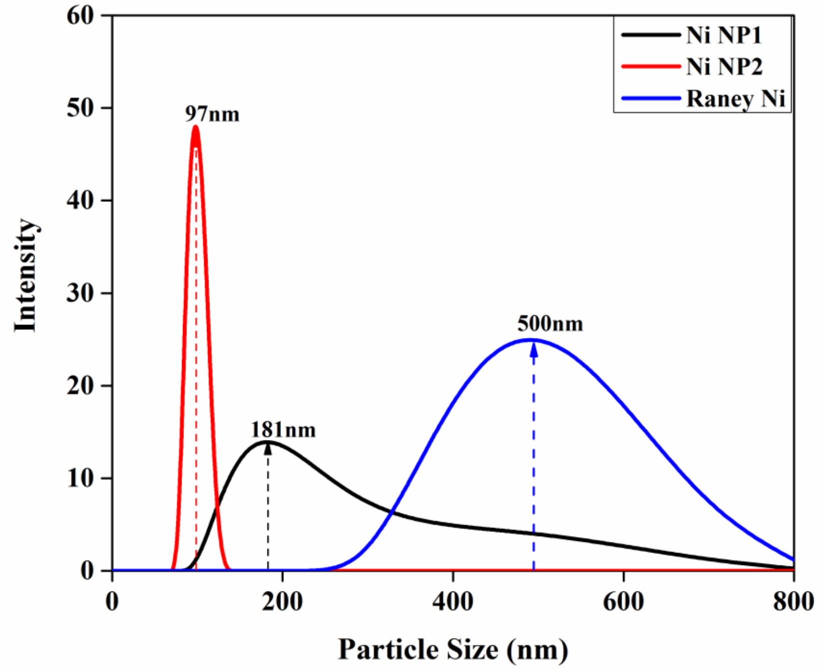


Fig. 7 DLS particle size distribution of synthesized Ni NP1, NP2 & Raney Ni

XRD analysis

The crystalline structure of synthesized nickel nanoparticles were studied by XRD pattern shown in Fig.8. The diffraction pattern clearly confirms the crystalline amorphous structure of the nanoparticles with face centered cubic (fcc) lattice. It is found that Ni NP1 is more crystalline than Ni NP2. The intense XRD peak for Ni NP1 were found at 44.5^{o}, corresponding to the plane (111) and some low intensity peaks were found to be at 51.9^{o} (200) and 76.5^{o} (311). Similar pattern was observed for Ni NP2 but one more low intensity peak was observed at (220).
Further the crystal structure was determined by using Scherrer equation and by taking FWHM of most intense peak at (111). The equation is as follows:

$\beta (2\theta) = K\lambda / L \cos\theta$; where β = FWHM
L = crystalline size
Λ = wavelength of X-ray
K = constant (0.9)

By using this equation, the estimated size of NP1 & NP2 was found to be 8nm and 14nm respectively.

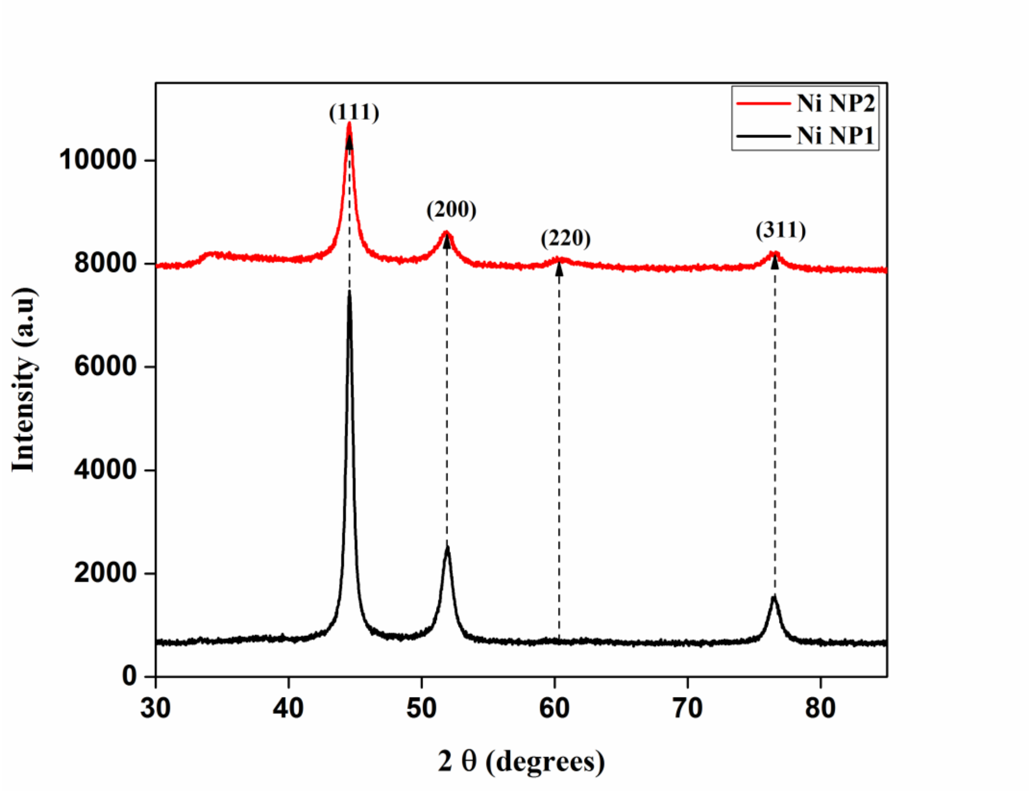
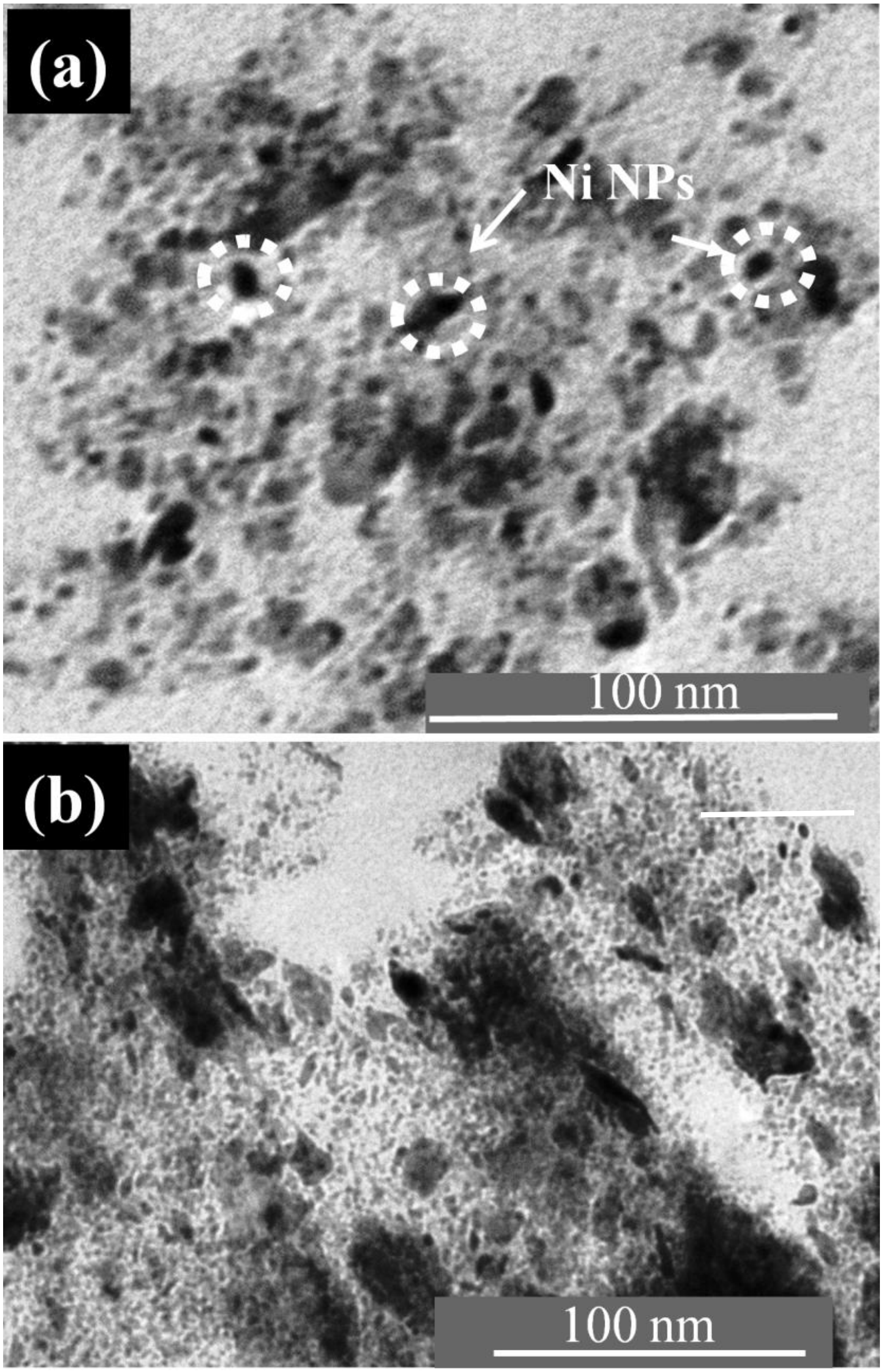


Fig. 8 X-Ray Diffraction (XRD) pattern of Ni NP1 & Ni NP2

TEM & SEM analysis

Fig.9 (a-d) represents the TEM images of synthesized Ni NP1.The shape was found to be irregular sphere morphology and Fig.10 (a-b) represents the SEM results of Ni NP2 showing wire like shape. It was observed that a little agglomeration occurred among Ni NP2 because of less amount of EG used for its synthesis. The average size shown by the TEM of Ni NP1 was found to be of diameter 17.5nm.


(a)
Ni NPs
100 nm
(b)
100 nm

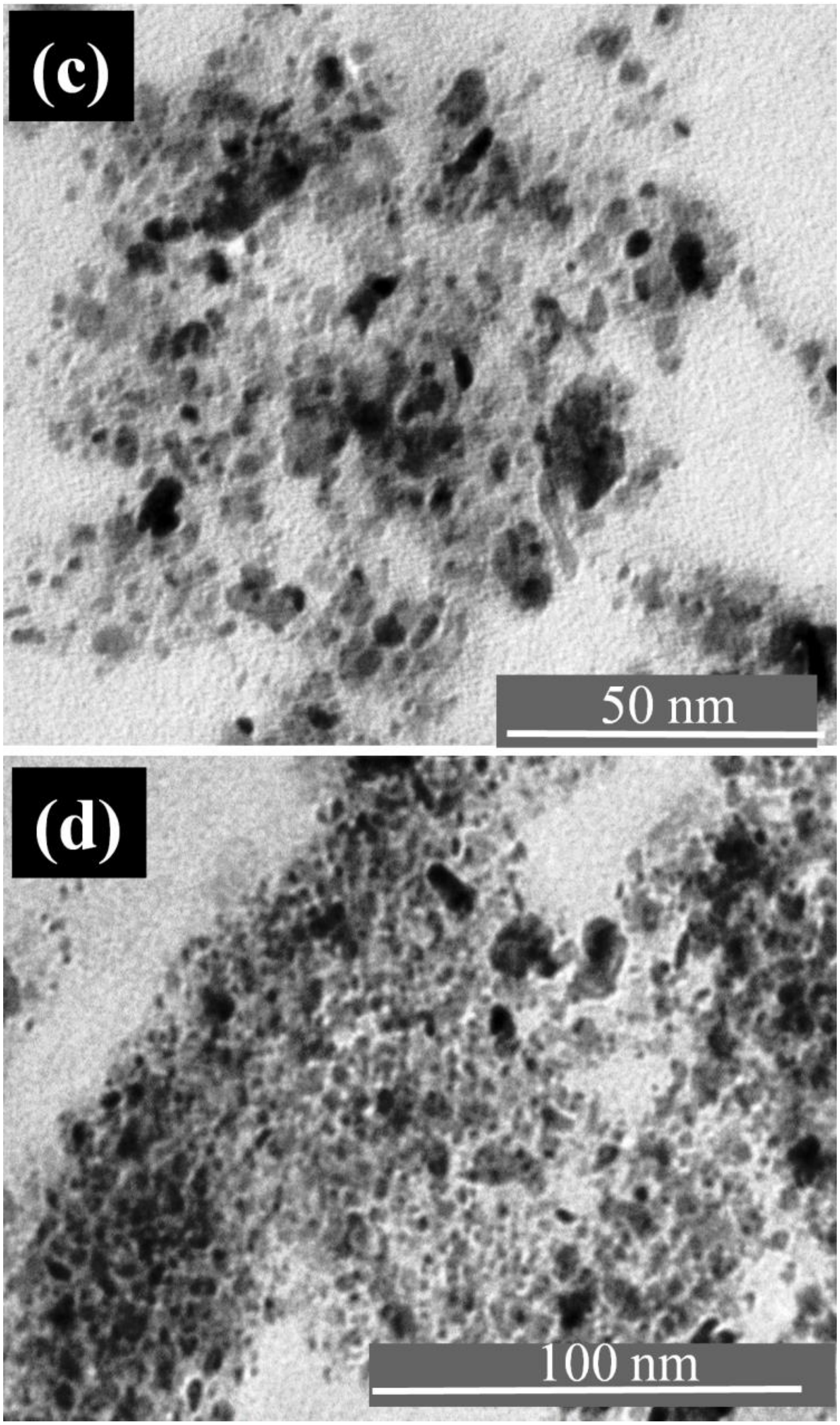


Fig.9 (a-d) TEM images of Ni nano spheres (NP1)

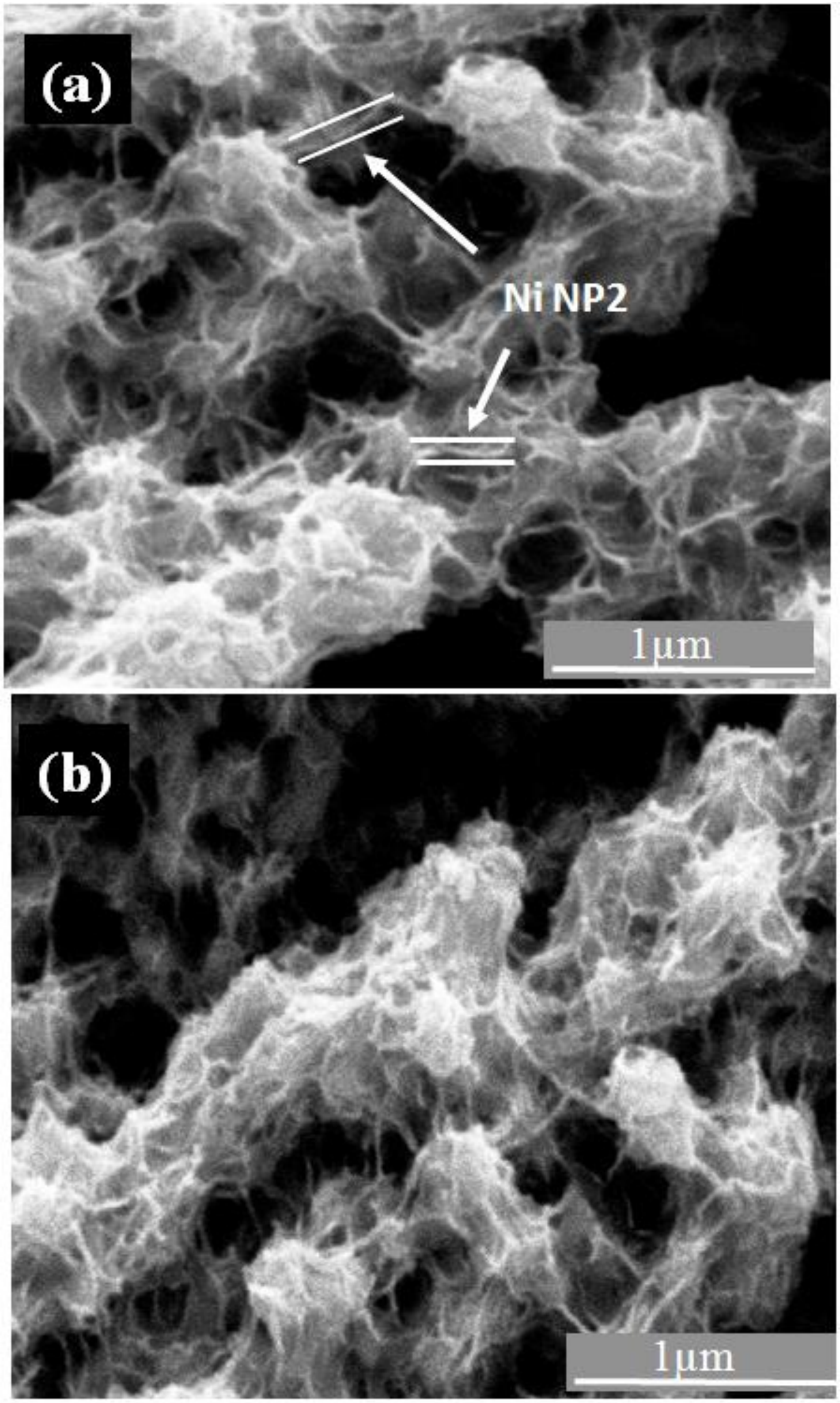


Fig.10 (a-b) SEM images of Ni agglomerated nanowires (NP2)

4.2.Catalytic studies of nickel nanoparticles

The catalytic activity of synthesized nickel nanoparticles NP1 and NP2 was investigated by carrying the reduction of p-nitro phenol (PNP) to p-amino phenol (PAP). 0.1Mm of PNP was taken as the initial concentration throughout the experiment.

(a)Catalytic activity of Ni NP1

First, we investigated the hydrogenation of PNP by Ni NP1.The reaction was initiated by addition of different amount of catalyst. 1mg, 3mg, 5mg and 7mg of catalyst was added for optimization. During the reaction, the absorption peak of PNP at 400nm disappeared and the new peak at 256nm was seen which confirms the formation of p-amino phenol (PAP). It was observed that with the addition of catalyst there was a color change from light yellowish-green to clear solution which indicated the completion of the reaction. The estimated time for the reaction to complete was found to be 60 minutes. Fig.11 (a) shows the UV-vis spectra of the reduction of PNP to PAP by Ni NP1 taken in different amount. Further, the %yield was calculated with respect to the amount of catalyst used. It was found that reaction initiated by 7mg Ni NP1 catalyst had high percentage yield of 89% as shown in Fig.11 (b).

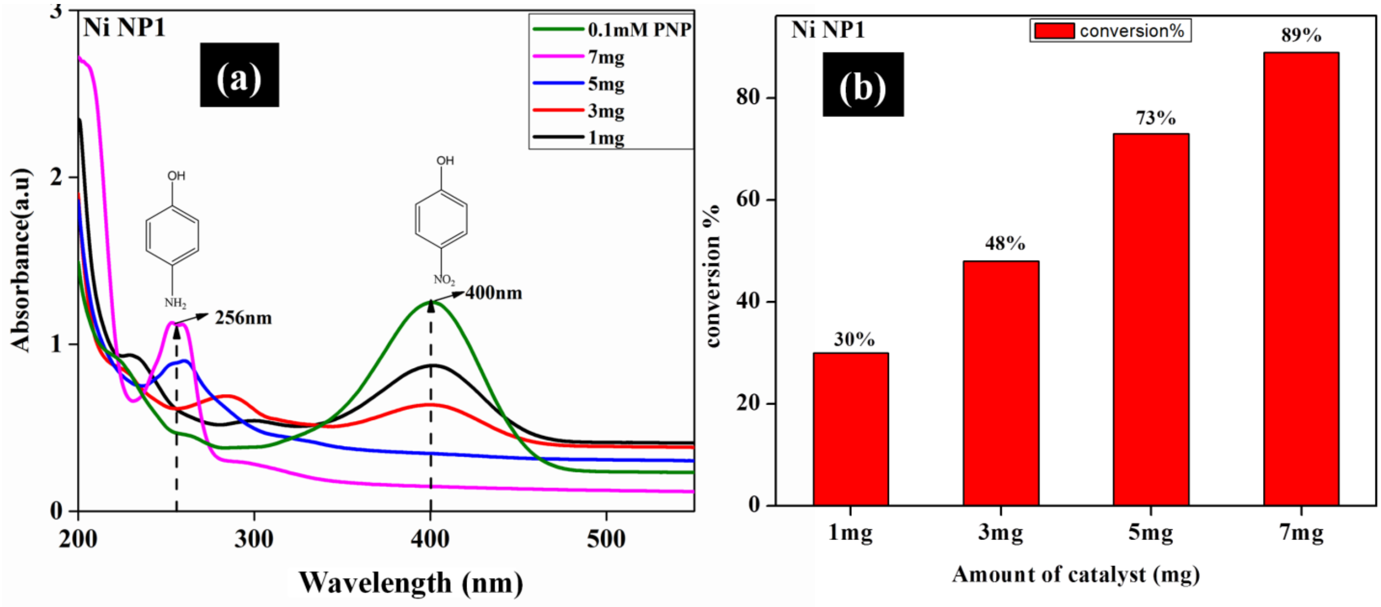


Fig. 11 (a) UV-vis spectra of hydrogenation of PNP to PAP by Ni NP1(b) Histogram showing %conversion of PNP to PAP by Ni NP1 with different amount of catalyst

(b). Catalytic activity of Ni NP2

Similarly, Fig.12 (a) represents the hydrogenation of PNP was carried out by Ni NP2 with same reaction conditions and parameters.0.1mM of PNP was taken and 3mg, 5mg & 7mg of Ni NP2 were added with three different reactions. It was found that the PNP absorption peak at 400nm was diminished and PAP absorption peak at 257nm was found with the color change of yellowish green to clear solution. Further it was observed that the reaction with 7mg Ni NP2 gave high percentage yield of 76% shown in Fig. 12(b). It was found that the conversion % of reduction of PNP to PAP by 7mg Ni NP1 was found to be more than Ni NP2.

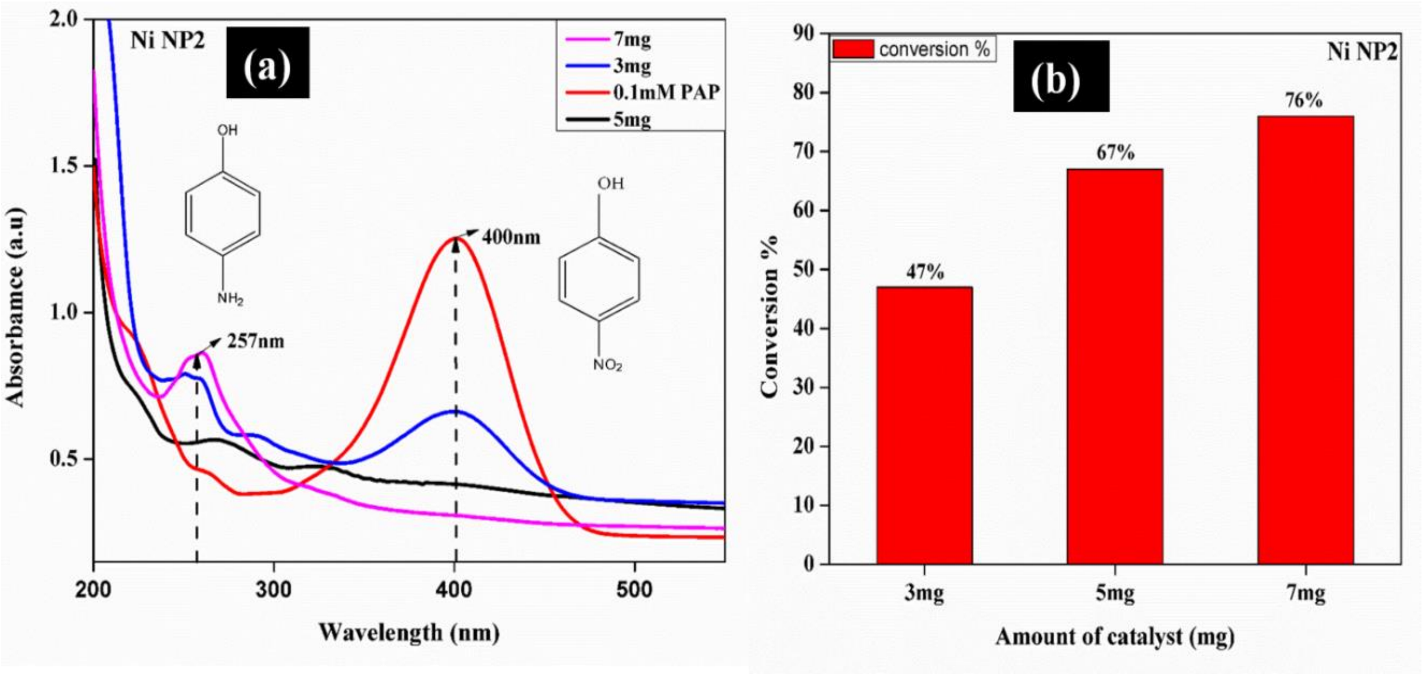


Fig.12 (a) UV-vis spectra of hydrogenation of PNP to PAP by Ni NP2 (b)Histogram showing %conversion of PNP to PAP by Ni NP2 with different amount of catalyst

(c) Comparative Time course study of hydrogenation of PNP to PAP by Ni NP1 & Ni NP2

In order to study and compare the better catalytic activity of prepared nano catalysts, time course reaction was investigated. By considering the above results, we analyzed the maximum conversion rate was given by 7mg Ni nano catalyst in both the NP1 & NP2. Therefore, time reactions were done by taking 7mg of Ni nano catalysts and the absorption studies were done at the time interval of 0min, 15min, 30min, 45min & 60min.Fig. 13(a) and 13(b) represents the time course reaction of reduction of PNP by Ni NP1 & Ni NP2 respectively.

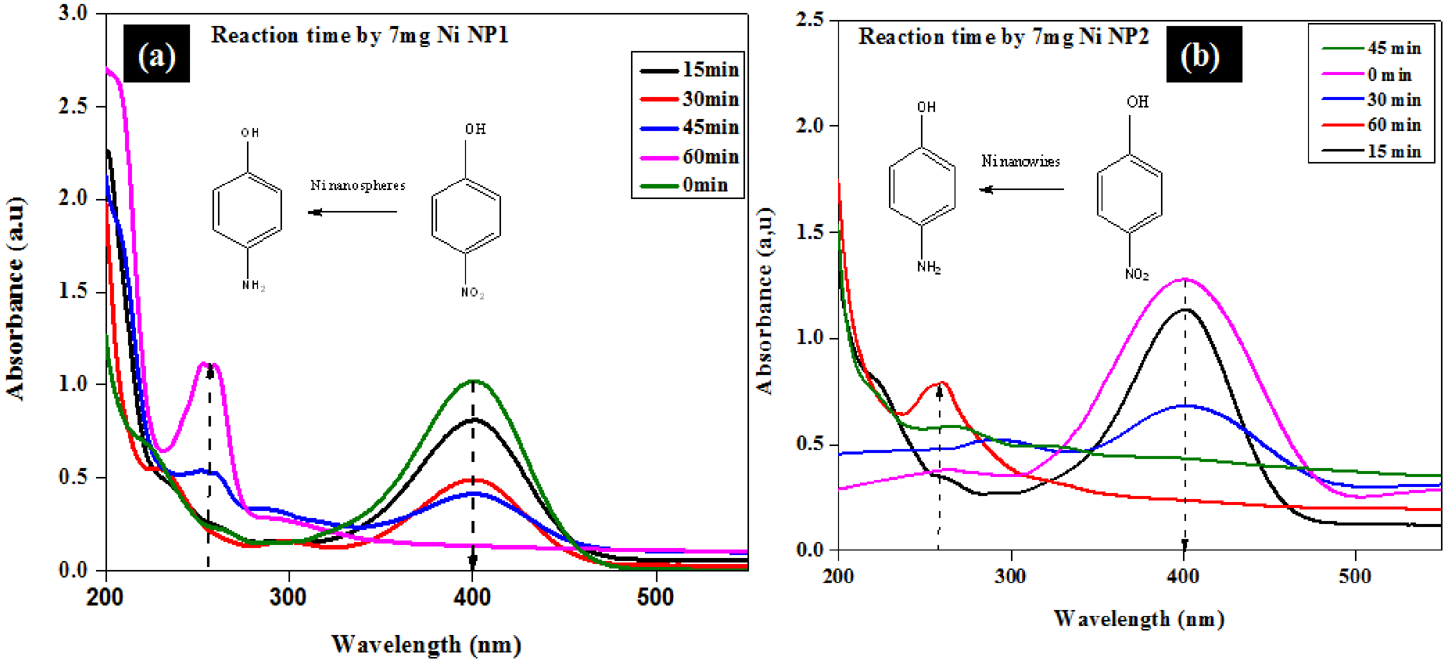


Fig. 13 (a) Absorption spectra representing time course study of reduction by Ni NP1 and (b) Ni NP2

(d) Comparative study of %yield and Kinetics of NP1 & NP2 with commercially available Raney Ni

The selective catalytic activity of Ni NP1 and Ni NP2 for reduction of nitro-aromatics was further studied by comparing its activity with commercially available Raney Ni. In the similar manner, different amount of Raney Ni in mgs was taken to reduce the p-nitro phenol and its %yield was compared with the %yield obtained by Ni NP1 & Ni NP2. It was found that superior catalytic activity was shown by Ni NP1 because of its highly crystalline structure, small size, large surface area and the solvent system used i.e. EG which prevented agglomeration. The kinetics studies reveal that reaction with NP1, NP2 and Raney Ni follows pseudo first order kinetics. The rate constants of NP1, NP2 & Raney Ni were 0.015 min^{-1}, 0.009 min^{-1} and 0.001 min^{-1} respectively. Hence the decreasing order for the rate constant values can be given as: NP1 > NP2 > Raney Ni. Fig.14 (a) shows the comparative % conversion with time graph for reduction of PNP by using 7mg NP1, NP2 & Raney nickel as catalyst. Fig. 14(b) shows the kinetics of reduction by 7mg NP1 NP2 & Raney nickel as catalyst.

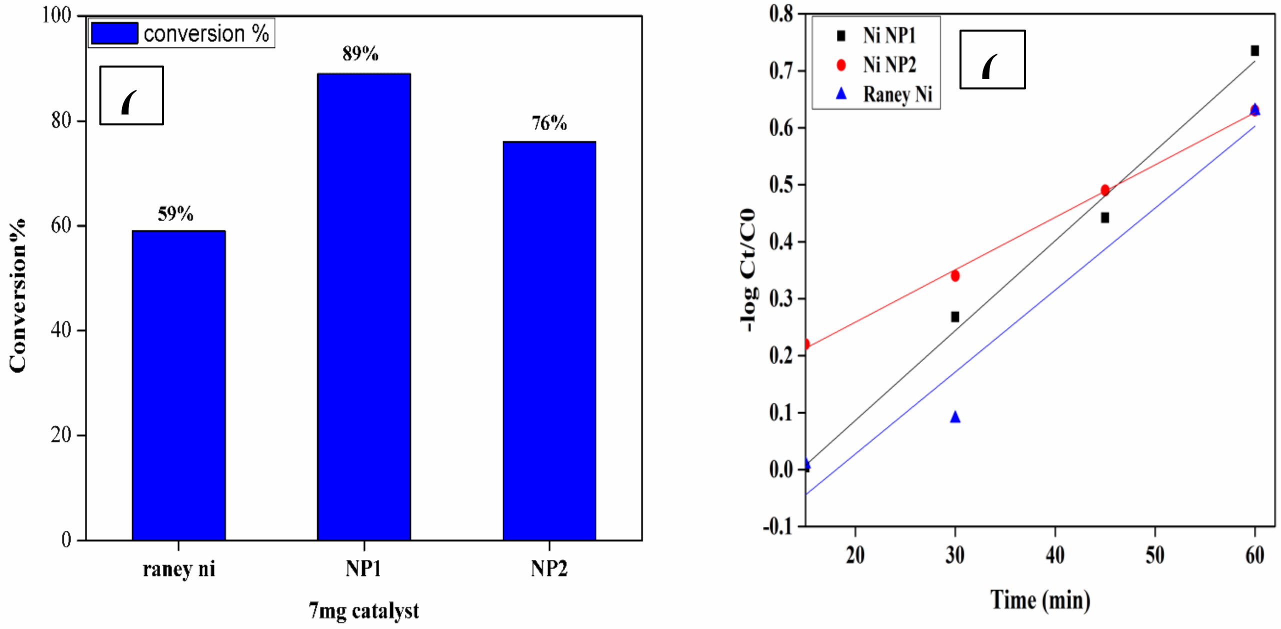


Fig.14 (a) Histogram showing comparative study of %conversion of PNP to PAP by taking 7mg NP1, NP2 & Raney ni as catalyst (b) Plot of logC0/Ct verses Time of Raney Ni. Ni NP1 & Ni NP2

(e) HPLC analysis

The chemical analysis of the reaction was confirmed by HPLC studies shown in Fig.15 (a-d). The retention time (t_R) for the reaction by 7mg catalyst with Ni NP1, Ni NP2 & Raney

Ni was found to be 9min, 10min and 12.5min assigned to the formation of amine. The results were compared with the standards which had the retention time of 18min which corresponds to nitro group.

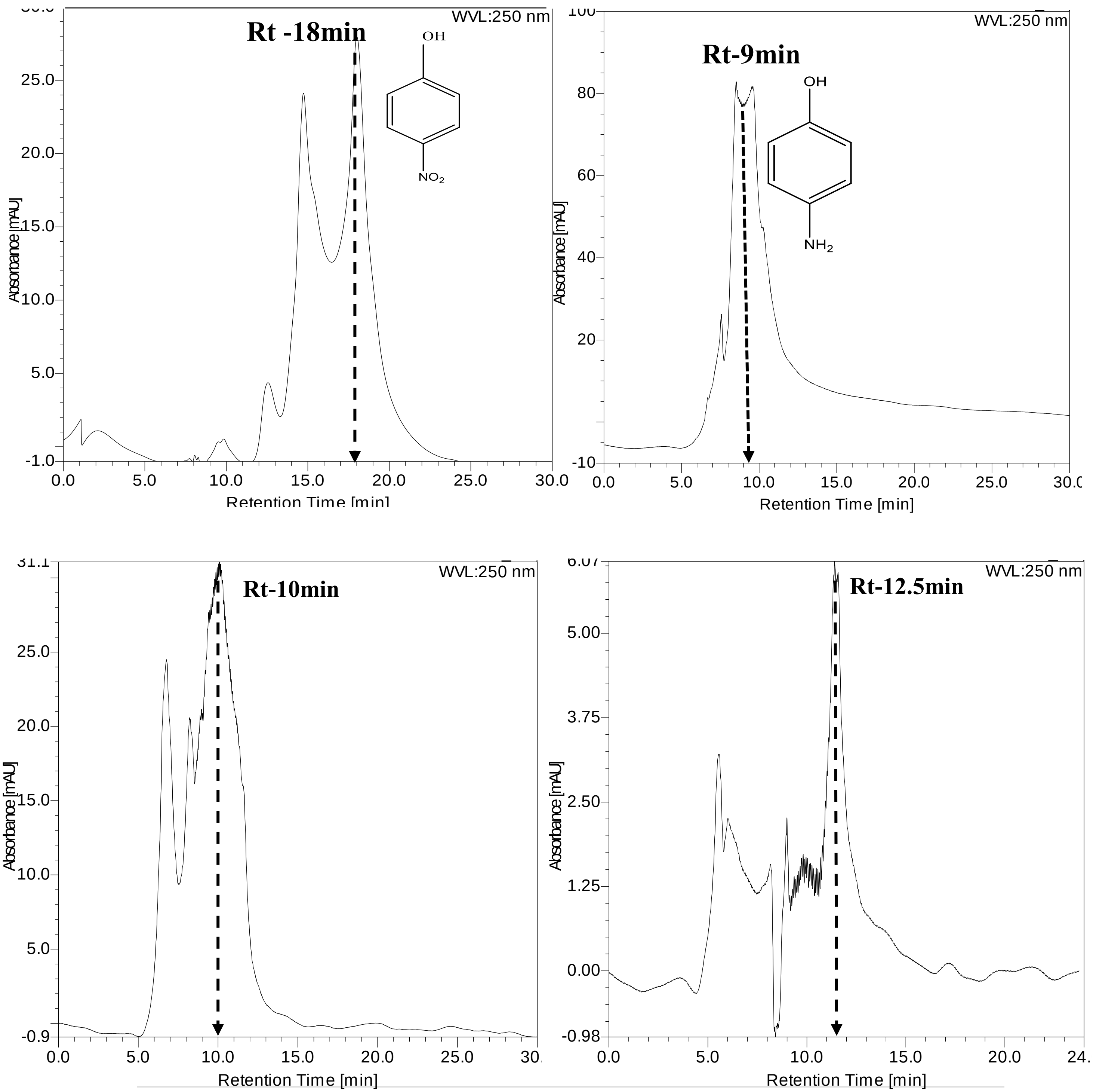


Fig. 15 HPLC spectra for hydrogenation of PNP to PAP [(a) Standard PNP (b)7mg Ni NP1 , (c) Ni NP2 , (d)Raney Ni

5. Conclusion

Nickel nanoparticles of different size and morphology were synthesized successfully. TEM & SEM results confirms the irregular sphere shape of NP1 and agglomerated wire shape for NP2.It was found that the Ni NP1 exhibited the better catalytic activity as compared to Ni NP2 & Raney Ni in hydrogenation of p-nitrophenol to p-aminophenol. The catalytic activity is increased because of small size of Ni NPs. Hence, the synthesized Ni NPs can work as a better catalyst for the improved hydrogenation of nitro-aromatics.

6. References

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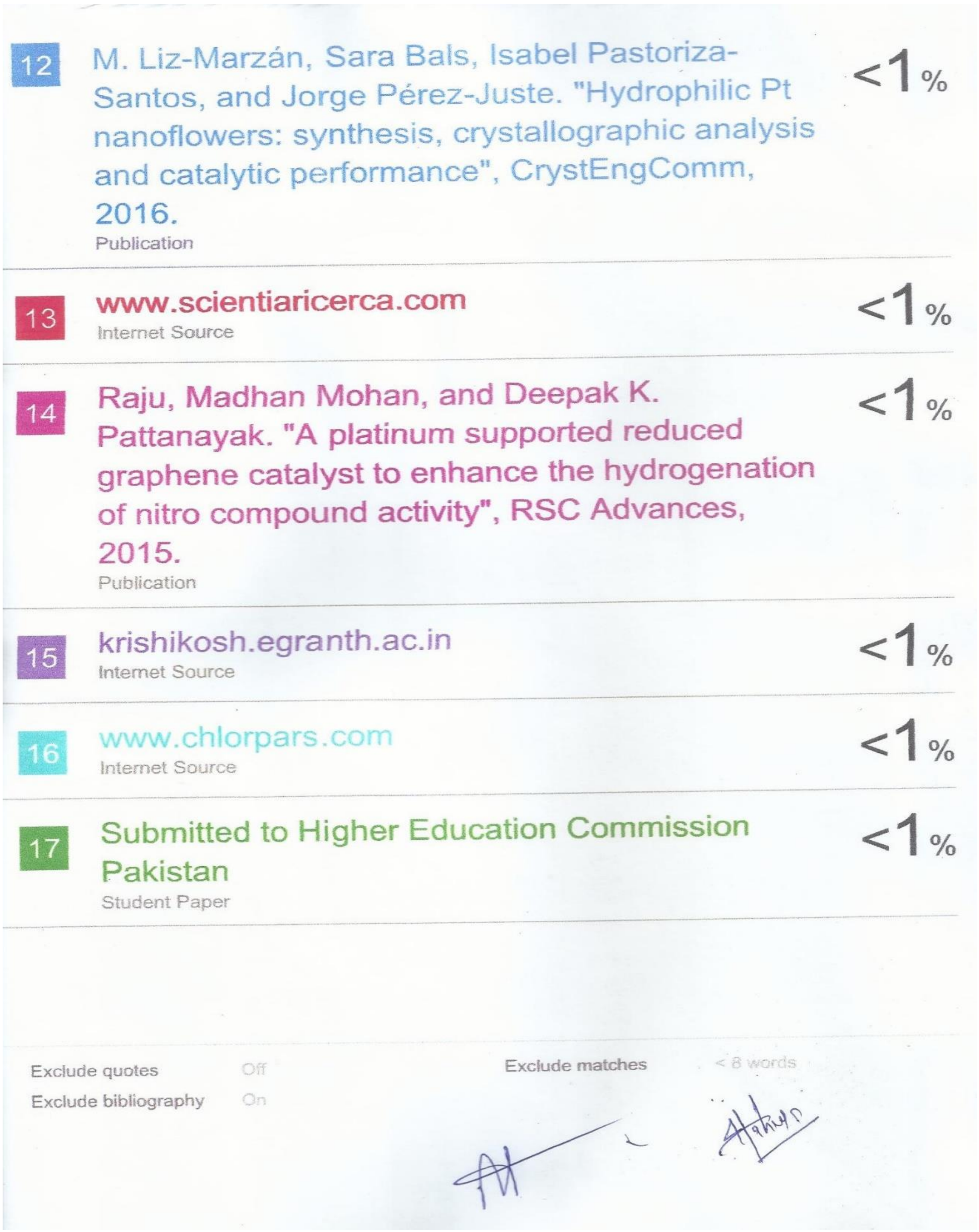

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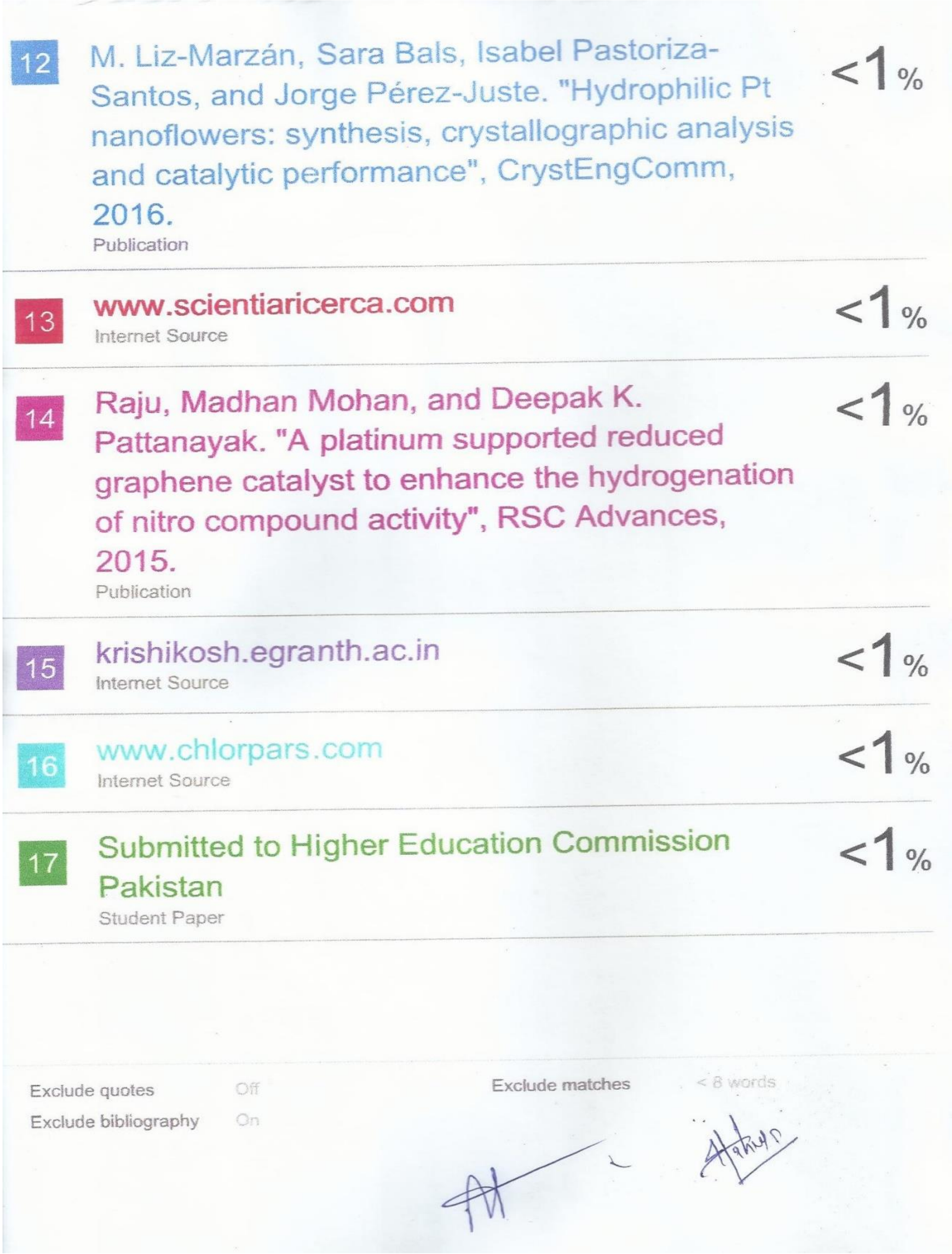

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