# Nickel Nanoparticles as Efficient Catalyst for Electron Transfer Reactions

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**Abstract** The catalytic efficiency of nickel nanoparticles was investigated in some electron transfer reactions. The nanoparticles brought about rapid room temperature reduction of a number of nitro aromatics in an aqueous medium with high chemoselectivity and also helped to speed up redox reaction of  $Fe(CN)_6^{-3}$  and  $S_2O_3^{-2}$ . In addition, interesting results were obtained for microwave assisted decolourization of azo dye. The reactions were monitored through UV–Vis spectroscopy. The present study has additional advantages of reusability of catalysts and aqueous medium. The ultimate goal was to assess the suitability of low cost nanocatalyst for electron transfer reactions under aqueous conditions.

**Keywords** Ni nanoparticles  $\cdot$  Ni catalyst  $\cdot$  *p*-Nitroaniline  $\cdot$  Azo dye  $\cdot$  Reduction  $\cdot$  Redox reaction

## 1 Introduction

Nanocatalysis is one of the rapidly developing areas in heterogeneous catalysis [1–5]. Strikingly novel catalytic

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properties including greatly enhanced reactivity [6] and selectivity [7] have been reported for metal nanoparticles (NPs) catalysts as compared to their bulk counterparts. In addition to noble metals, nanoparticles of nickel (NiNPs) also have proved as catalysts for various organic reactions [3] including the chemo selective oxidative coupling of thiols [7], reduction of carbon–carbon multiple bonds [8, 9], imine reduction [10], hydrodehalogenation of organic halides [11], reduction of sulfonates and aromatic compounds [12], homocoupling of aryl iodides [13], Wittigtype olefination [3],  $\alpha$ -alkylation of methyl ketones with primary alcohols [14], reduction of aldehydes and ketones [15, 16], and supports for hydrogen adsorption [17, 18].

The reduction of aromatic nitro compounds to the corresponding amines is important in synthetic chemistry because aromatic amines are frequent intermediates in the production of pharmaceuticals, agrochemicals, polymers, dyes, and other fine chemicals [19]. A variety of procedures and reducing agents are available for this purpose [20]. In literature a few procedures involving noble metal NPs such as Pd, Pt, Ag, Au, as well as Cu, and Ni NPs have been demonstrated for the reduction of nitro group [20-22]. The main limitations of earlier reported work were the necessity of high H<sub>2</sub> pressures, organic solvents and high temperatures. Further, the selection of metal and its support, the hydrogen source and operational simplicity, which are the important parameters for effective conversions, are restricted. However, an alternative efficient, simple, chemoselective, green and cost-effective procedure is highly appreciated.

The role of metal nanoparticles is very important in redox reactions and can be explained in terms of electrochemical potentials [23]. The considerable catalytic activity for the NiNPs can be probably attributed to the following two factors: (1) larger surface than a bulk metal to simultaneously accommodate both the oxidation and reduction half reactions and (2) NiNPs could provide a much higher activity than a bulk metal due to the size effect. In other words, the superior catalytic activity of the NiNPs is a result of two effects: good electrical connection and small sizes related to their bulk part.

In the past our group has focused on biological and catalytic applications of metallic NPs of Ag, Cu and Ni [24–26]. The present work highlights the use of NiNPs as catalyst for three different kinds of reactions. (1) Selective hydrogenation of aromatic nitro compounds at room temperature (RT) in aqueous medium, (2) Microwave (MW) assisted azo dyes reduction by ascorbic acid (AA) and (3) Electron transfer reaction between potassium ferricyanide (PFC) and sodium thiosulfate (STS).

### 2 Experimental

### 2.1 Materials and Methods

*para*-Nitroaniline (PNA), other aromatic nitro compounds, potassium ferricyanide (PFC), sodium thiosulfate (STS), ascorbic acid (AA) and azo dyes were all purchased from Merck Mumbai, India. All the solutions were prepared using double-distilled and demineralized water.

NiNPs were synthesized through a wet chemical reduction process using Ni(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O and soluble starch as metal salt precursor and stabilizing agent respectively. NaBH<sub>4</sub> (10 %, W/V) was used as reducing agent and liquid ammonia as complexing agent. Briefly 0.4 mL of 1 M nickel acaetate solution was added to 10 mL of starch solution (1 %, W/V) and stirred on a magnetic stirrer at RT. The pH of the solution was adjusted to 10 with liquid ammonia and reduction was carried out with 0.6 mL of 10 % NaBH<sub>4</sub> solution. The NPs were isolated by centrifugation and dried under vacuum [26]. Characterisation of starch capped NiNPs has been discussed in our previous paper [26]. Energy dispersive X-ray (EDX) analysis of the vacuum dried NiNPs was recorded by model-JSM-5610 LV attached to scanning electron microscopy (SEM). Surface area and porosity of the samples were measured by a volumetric adsorption system (Micromeritics Instrument Corporation, USA, model ASAP 2010) using N2 adsorption/ desorption isotherms at 77 K up to 1 bar. Prior to the measurements, the samples were activated (degassed) by heating at the rate of 1 K/min up to 383 K under vacuum. The temperature as well as vacuum was maintained for 7 h prior to the measurements. The surface area was calculated by Brunauer-Emmet-Teller (BET) method while the porosity by Barrett-Joyner-Halenda (BJH) method.

NiNPs catalyzed hydrogenation, decolourization of dye and redox reactions were monitored on PerkinElmer Lambda 35 UV–Vis spectrophotometer by corresponding  $\lambda$ -max. Hydrogenation reaction monitoring was also done by thin-layer chromatography (TLC, Using ninhydrin as staining reagent) and gas chromatography (GC). All products of the reduction of nitroarenes are commercially available and were identified by comparing their physical and spectral data (m.p., TLC (silica gel 60 F254, Merck, Mumbai, India), GC (Perkin Elmer clarus 500 GC) and <sup>1</sup>H NMR (BRUKER 400 MHz) with those of authentic samples or reported data (data not shown). For decolourization of azo dyes microwave (MW) oven operated at the 100 % power of 1350 W and frequency 2,450 MHz.

# 2.2 Catalytic Reduction of *p*-Nitroaniline and Other Aromatic Nitro Compounds

In a typical reaction PNA (0.0036 mol) was used as a starting material, NaBH<sub>4</sub> (0.0260 mol) as a source of hydrogen, water (6 mL) as solvent and NiNPs 50 mg (10 wt% of PNA, 0.85 mmol) as catalyst. All the components were mixed together in 50 mL round bottom flask and the reaction was carried out at room temperature (RT, 25-30 °C) under stirring for 90 min.

The product was isolated by extraction in dichloromethane and evaporation of solvent followed by column chromatography (10:90, ethyl acetate in hexane v/v) over basic alumina furnished PPDA. The spectroscopic data of this compound are in good agreement with those reported. The reaction was also carried out in absence of NiNPs for comparison.

Reduction of other nitro aromatics was carried out in a similar manner. The products purified by short-path basic alumina chromatography (0–40 % ethyl acetate in hexane v/v) were analyzed by <sup>1</sup>H NMR (data not given).

### 2.3 Decolourization of Azo Dye

Experiments were carried out by using four different kinds of azo dyes. The dyes used were Orange II (OR-II), Methyl Red (MR), Methyl Orange (MO), Erichrome Black-T (EBT) and mixture of dyes (MD). Each microwave (MW) assisted reduction experiments were carried out by taking 6 mg of NiNPs (0.102 mmol) into 50 mL stoppered borosilicate Erlenmeyer flasks together with 5 mL of an aqueous solution with  $6.5 \times 10^{-4}$  mol L<sup>-1</sup> of azo dyes and  $3 \times 10^{-3}$  mol L<sup>-1</sup> ascorbic acid (AA). Analogous experiments were performed without AA, NiNPs and alternatively without MW irradiation (at RT, 25–30 °C). The decolourization of each dye was measured by its absorbance at  $\lambda_{max}$ using UV–Vis spectrophotometer. Reduction of a mixture of dyes was also attempted in a similar manner.

#### 2.4 Redox Reaction

The reaction mixture containing as synthesized NiNPs (5 mg, 0.085 mmol), 1 mL of 0.001 mol potassium ferricyanide (PFC) and 1 mL of 0.1 mol sodium thiosulfate (STS) was placed in a quartz cell with 1 cm<sup>3</sup> path length. The reaction was monitored by UV–Vis spectroscopy in the presence and absence of NiNPs at  $25 \pm 2$  °C temperature.

All experiments have been repeated three times and the reproducibility confirmed. The recyclability of the NPs was also surveyed. The NPs were recovered by centrifugation, washed with acetone, dried at 60  $^{\circ}$ C under vacuum and used for the next reaction.

# **3** Results and Discussion

Energy dispersive X-ray analysis (EDX) indicates that the well-cleaned final product is mostly composed of Ni, with no other signal (supporting information). The Brunauer–Emmet–Teller (BET) surface area of a NiNPs sample was determined to be  $17.0745 \text{ m}^2 \text{ g}^{-1}$  (supporting information). NiNPs have high surface area which is greatly differs from that obtained for NiNPs synthesised from the electric explosion of wire, the specific area of which was 4.405 m<sup>2</sup> g<sup>-1</sup> [27]. The pore size of the NPs was determined to be 12.3703 nm by the Barrett–Joyner–Halenda (BJH) analysis of the isotherms (supporting information). The total pore volumes were 0.052804 cm<sup>3</sup> g<sup>-1</sup>.

# 3.1 Catalytic Reduction of *p*-Nitroaniline and Other Aromatic Nitro Compounds

Metal nanocatalyst can catalyze the reduction of nitro compounds by acting as an electronic relay system to overcome the kinetic barrier, in which the electrons donated by BH<sub>4</sub> can be transferred to the acceptor nitro groups [28]. In the present case hydrogenation of PNA as a model system was used to study the efficiency of the NiNPs as catalyst in aqueous medium (Scheme 1). The results of the conversion of PNA to PPDA are illustrated in Table 1. It is seen from the table (entries 1-3) that the presence of a catalyst along with NaBH<sub>4</sub> is required for hydrogenation of PNA. The optimum reaction conditions for PNA reaction are given in Table 1 (entry 7), which yields  $95 \pm 2$  % of product at RT after 90 min and selectivity was 100 %.

This reaction was monitored by UV–Vis spectrophotometer (Fig. 1), where the product and reactant show different absorption bands at 307 and 381 nm, respectively. As shown in Fig. 1, when the reaction conditions mentioned in Table 1 (entry-7) was used, the reaction



**Scheme 1** Schematic representation of the performance of NiNPs as catalysts in the reduction of PNA to PPDA by NaBH<sub>4</sub> in water

**Table 1** Optimization of reaction conditions for hydrogenation of *p*-Nitroaniline

S. no.	Catalyst (mg)	NaBH <sub>4</sub> (mol)	Temperature (°C)	Time (h\min)	% Yield <sup>b</sup>
1	None	None	25-30 to reflux	24 h	_
2	50	None	25-30 to reflux	24 h	_
3	None	0.0260	25-30 to reflux	24 h	<5
4	50	< 0.005	25-30 to reflux	24 h	<10
5	50	0.007	25-30 to reflux	24 h	$31\pm5$
6	50	0.0132	25-30	180 min	$95\pm3$
7 <sup>a</sup>	50	0.0260	25-30	90 min	$95\pm3$
8	50	0.0260	50-60	60 min	$95\pm3$
9	50	0.0260	70-80	15 min	$95\pm3$
10	10	0.0260	25-30	300 min	$95\pm3$
11	20	0.0260	25-30	300 min	$95\pm3$
12	30	0.0260	25-30	300 min	$95\pm3$
13	40	0.0260	25-30	180 min	$95\pm3$
14	≥50	0.0260	25-30	90 min	95 ± 3

Reaction conditions p-Nitroaniline 0.0036 mol, solvent (water) 6 mL

<sup>a</sup> Optimized reaction condition

<sup>b</sup> Isolated yield



**Fig. 1** UV–Vis spectra indicating the change of *p*-nitroaniline to *p*-phenylenediamine in presence of NiNPs

proceeded faster within 90 min and the  $\lambda_{max}$  shifted from 381 to 307 nm. Whereas, in the absence of NiNPs, the peak at 381 nm corresponding to PNA did not disappear even after 24 h of reflux.

Furthermore, experiments were performed using a different mole ratio of NaBH<sub>4</sub> in standard reaction. On using NaBH<sub>4</sub> less than 0.005 mol, reaction yield was less than 10 % even after 24 h of reflux (Table 1, entry 4). When we increased moles of NaBH<sub>4</sub> from 0.005 to 0.007, the yield increased to  $31 \pm 5$  % (Table 1, entry 5), whereas using 0.0132 mol of NaBH<sub>4</sub> resulted into a remarkable yield (95 ± 2 %) at 35 °C within 180 min (Table 1, entry 6). However, lowering the amount of NaBH<sub>4</sub> caused an increase in the reaction time and hence an adequate quantity of NaBH<sub>4</sub> was used in optimum reaction condition. Good to high yields were obtained at 80 °C temperature and the reaction temperature increases, reaction time decreases (Table 1, entries 8, 9).

Variation in quantity of NPs (Table 1, entries 10–14) under optimum reaction conditions showed that even 10 mg was sufficient for catalyzing the reaction at RT but took 300 min for maximum conversion (Table 1, entry 10). On the other hand with 40 mg the reaction time decreased to 180 min (Table 1, entry 13). Beyond 50 mg the reaction time and yield did not change (Table 1, entry 14).

Under the optimized conditions, we investigated the scope of converting various aromatic nitro compounds to aromatic amines by using NiNPs, NaBH<sub>4</sub> and water (Scheme 2). NiNPs was applied for all substrates and they almost gave same yield in similar reaction time (Table 2). The results were satisfactory for various aromatic nitro substrates with different functional groups (Table 2). Further, this catalytic system works efficiently in aqueous system and therefore no hazardous solvent was required. This reaction has been investigated in the presence of other protic solvents such as methanol, ethanol, and ethylene glycol; however, none of them gave satisfactory results (data not given). In an aqueous system NaBH<sub>4</sub> gives sodium metaborate (NaBO<sub>2</sub>) [29] which is the only waste generated during the reaction. However sodium metaborate can be recycled using magnesium hydride (MgH<sub>2</sub>) or magnesium silicide (Mg<sub>2</sub>Si) by annealing (350-750 °C)



R: -OH, -NH<sub>2</sub>, -OCH<sub>3</sub>, -Cl, -I, -Br, -CH<sub>3</sub>, -CH<sub>2</sub>OH, -C<sub>4</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>3</sub>N

Scheme 2 General scheme for reduction of various nitro aromatics

under high  $H_2$  pressure (0.1–7 MPa) for 2–4 h [29]. This opens up new possibilities for eco-friendly synthesis of aromatic amines.

# 3.2 Decolourization of Azo Dyes

Degradation of dyes, especially azo dyes which contribute to about 70 % of all used dyes, is difficult due to their complex structure and synthetic nature [30]. The most commonly used method is adsorption which causes the high operational cost because regeneration is generally not so effective [31]. The use of noble metal NPs like Pd [32]. Au [33], Ni [34] and Ag [35] in dye decolourization or reduction has been reported. This is the first report on the MW assisted decolourization reaction of azo dye by NiN-Ps. As a representative case, the catalytic activity of NiNPs was first investigated in the decolourization of Orange II (OR-II) in MW, a kind of azo dye with -N=N- bonds. UV-Vis spectra in Fig. 2 shows that before the addition of NiNPs, there was the maximum absorption band centered at 483 nm, which could be assigned to the conjugated system formed by the -N=N- bonds of OR-II. The colour of the dye is attributed to this maximum absorption band, which could be used to monitor the decolourization reaction. Ascorbic acid alone could not induce complete decolourization of the dye in MW. But when irradiated in presence of NiNPs ascorbic acid led to complete decolourization of the dye. The absorption band at 483 nm decreased and disappeared, which could be ascribed to the loss of conjugation of -N=N- bonds due to electron transfer through surface of NiNPs (Scheme 3). As discussed by Pande and co-workers [36], when the size of bulk metals goes to the nanoscale, electron transfer is efficient, in addition to large surface area. Thus the electron transfer between the dye and ascorbic acid occurs before rapid diffusion pulls them apart [37].

Although the role of starch is only to cap the NiNPs and prevent its oxidation [26] its role as adsorbent needs to be assessed in the present case since starch is highly active towards adsorption of dye molecules [38]. To rule out the possibility of adsorption, a control experiment was performed with only starch. No significant decrease in the absorbance was observed indicating that the decolourization is not simply due to dye adsorption onto the support. Also under MW condition adsorption will not occur due to the high kinetic energy of dye molecules.

Similarly, in the study of decolourization of other azo dyes with AA, it was noted that the absorption peak at corresponding wavelength ( $\lambda_{max}$ ) (Table 3) of all azo dyes significantly decreases indicating that NiNPs catalyzes the decolourization of azo dyes.

The experiment was also successful with a mixture of dyes. In all experiment decolourization occurred within

Table 2Selective reduction ofNitro aromatics to aromaticamines in water with NiNPs atRT

S. no.	Substrate	Product	Time	Yield <sup>a</sup> $(0/2 + 2)$	Selectivity
			(11111)	(% ±3)	(%)
1	o-Nitrophenol	o-Aminophenol	80	90	100
2	p-Nitrophenol	p-Aminophenol	80	95	100
3	<i>m</i> -Nitrophenol	<i>m</i> -Aminophenol	100	95	100
4	o-Nitrotoluene	o-Toulidine	120	85	100
5	p-Nitrotoluene	<i>p</i> -Toulidine	120	90	100
6	<i>m</i> -Nitrotoluene	<i>m</i> -Toulidine	100	90	100
7	p-Nitrobenzyl alcohol	p-Aminobenzyl alcohol	120	92	100
8	m-Nitrobenzyl alcohol	m-Aminobenzyl alcohol	120	91	100
9	o-Nitrobenzyl alcohol	o-Aminobenzyl alcohol	130	94	100
10	4-Chloro-3-nitro aniline	4-Chlorobenzene-1,3-diamine	150	90	100
11	4-Chloro-2-nitro aniline	4-Chlorobenzene-1,2-diamine	140	90	100
12	Nitrobenzene	Aniline	180	95	100
13	o-Nitroaniline	o-Phenylenediamine	90	95	100
14	<i>m</i> -Nitroaniline	<i>m</i> -Phenylenediamine	95	94	100
15	p-Nitroaniline	p-Phenylenediamine	90	95	100
16	o-Chloronitobenzene	o-Chloroaniline	100	95	100
17	m-Chloronitobenzene	<i>m</i> -Chloroaniline	100	94	100
18	p-Chloronitobenzene	<i>p</i> -Chloroaniline	90	95	100
19	o-Bromonitobenzene	o-Bromoaniline	110	96	100
20	m-Bromonitobenzene	<i>m</i> -Bromoaniline	110	95	100
21	1-Methoxy-3-nitrobenzene	3-Methoxyaniline	80	96	100
22	1-Methoxy-2-nitrobenzene	2-Methoxyaniline	80	97	100
23	1-Iodo-4-nitrobenzene	4-Iodoaniline	100	94	100
24	6-Nitroquinoline	Quinolin-6-amine	130	90	100
25	1-Nitronaphthalene	1-Naphthylamine	140	91	100
26	2-Nitronaphthalene	2-Naphthylamine	160	90	100
27	3-Nitroquinoline	Quinolin-3-amine	180	92	100

Reaction conditions Substrate 0.0036 mol, catalyst 10 wt% (0.85 m mol) of Substrate, sodium borohydride 0.0260 mol and solvent (water) 6 mL

<sup>a</sup> Isolated yield after column chromatography and reactions were carried at RT



Fig. 2 UV-Vis spectra related to experiments on decolourization of OR-II dye under different conditions. *Inset* shows related digital photograph

2–4 min (Table 3). The process is extremely slow at RT (Supporting information) irrespective of the presence of NP while it was feasible in a very short time on MW irradiation.

This suggests that both NiNPs and MW play an important role in the decolourization of dye.

# 3.3 Redox Reaction Between Potassium Ferricyanide and Sodium Thiosulfate

It has been reported that the electron transfer reaction between  $Fe(CN)_6^{-3}$  and  $S_2O_3^{-2}$  is catalyzed by noble metal like Pt [39, 40]. The redox reaction proceeds by electron transfer through the surface of the PtNPs, where they act as highly dispersed electrodes. We attempted this reaction for the first time in presence of NiNPs which are economically more viable. The characteristic absorption of  $Fe(CN)_6^{-3}$  was observed at 420 nm. When reaction takes place

Scheme 3 Schematic representation of the performance of NiNPs as catalysts in the electron transfer reaction between ascorbic acid and Orange II for decolourization of dye



Table 3 Name, corresp  $\lambda_{max}$  (nm), decolourizati and structure of dyes

$\lambda_{\text{max}}$ (nm), decolourization time	Name of dyes <sup>a</sup>	$\lambda_{max} \; (nm)$	Decolourization time (s)	Structure of dye
and structure of dyes	Orange-II (OR-II)	483	120	O S-ONa N=N OH
	Methyl orange (MO)	465	220	
	Methyl red (MR)	427	195	H <sub>3</sub> C <sub>N</sub> COOH
<ul> <li><sup>a</sup> Reaction conditions: NiNPs</li> <li>6 mg (0.102 mmol), aqueous solution of azo dyes 2.5 mL</li> </ul>	Erichrome black-T (EBT)	540	190	NO <sub>2</sub> O SONa OH OH
$(6.5 \times 10^{-4} \text{ mol } \text{L}^{-1})$ and ascorbic acid 2.5 mL $(3 \times 10^{-3} \text{ mol } \text{L}^{-1})$ and MW	Mixture of dyes (MD)	456	190	-

between  $Fe(CN)_6^{-3}$  and  $S_2O_3^{-2}$  intensity of corresponding peak (420 nm) decreased with time. In both reactions absorption was measured at 3 min time intervals. In presence of NiNPs (Fig. 3a) there was a continuous decrease in absorbance at 420 nm with respect to time and after 27 min, peak completely disappeared. Whereas, in absence of NiNPs reaction proceeds very slowly and takes 6 h for its completion (Fig. 3a, inset). On the other hand, using PtNPs with the same concentration the reaction remained incomplete even after 40 min [39, 40]. Therefore, it can be said that in presence of NiNPs redox reactions proceeds faster owing to efficient electron transfer due to the larger surface area of NiNPs. The pseudo first-order plot of lnA420 against time showed a linear relationship with a

**Fig. 3 a** UV–Vis spectra indicating change of  $Fe(CN)_6^{-3}$  concentration during the reaction between  $Fe(CN)_6^{-3}$  and  $S_2O_3^{-2}$  at  $25 \pm 2$  °C in the presence of NiNPs, and the *inset* shows the UV–Vis spectra of an uncatalyzed reaction in the absence of NiNPs. **b** Pseudofirst-order plot of  $-lnA_{420}$ against time for the determination of the rate of reaction between  $Fe(CN)_6^{-3}$  and  $S_2O_3^{-2}$  using NiNPs



 Table 4
 Recycling experiments of hydrogenation of p-Nitroaniline at RT in optimum condition

Cycle	Reaction time (min)	% Yield (isolated, $\pm 3$ )	Selectivity (%)
1	90	95	100
2	90	95	100
3	90	94	100
4	110	94	100
5	120	95	100
6	140	95	100
7	180	94	100

**Table 5**Recycling experiments of decolourization of OR-II azo dyeby NiNPs in MW

Cycle	1	2	3	4	5
Time (s)	120	125	140	160	200

 
 Table 6
 Recycling experiments of redox reaction between PFC and STS by NiNPs

Cycle	1	2	3	4	5
Time (min)	27	28	30	30	42

correlation coefficient of 0.9027 (Fig. 3b). The rate constant value of the reaction, in the presence of the NiNPs, obtained from the slope of the straight line, was observed to be  $0.0028 \text{ min}^{-1}$ . These results were comparable with the results obtained using PtNPs [40].

#### 3.4 Recycling of NiNPs

The recyclability of the NPs was also surveyed in optimum condition for all three reactions (Tables 4, 5, 6). It was observed that the catalyst could be reused directly without further purification for seven consecutive runs in case of PNA to PPDA (Table 4). Up to three cycles there was no loss in activity. After that the reaction time increased in each successive recycling experiment reaching from 90 to 180 min finally after the 7th experiment. This may be due to gradual loss of the catalytic activity of NiNPs with the number of runs for various reasons mentioned in our previous work [26]. Similarly in case of decolourization of azo dye (Table 5) and redox reaction between PFC and STS (Table 6) was observed that the catalyst could be reused directly without further purification for five consecutive runs in both cases although reaction time increases.

### 4 Conclusions

The present study illustrates simple, green, convenient and technologically significant method for the synthesis of nickel nanoparticles in aqueous medium. These nanoparticles exhibited an excellent catalytic activity at room temperature reduction of aromatic nitro compounds in aqueous medium. The catalyst used here is economic and eco-friendly as it requires neither higher temperature nor harsh acid or bases, and produces higher yields with excellent chemoselectivity in reduction of nitro aromatics substrates. NiNPs also helped in speeding up decolourization of azo dyes and changed the order of a redox reaction. Recycling experiments demonstrated that the catalyst can be reused for successive runs.

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# References

- 1. Yan N, Xiao C, Kou Y (2010) Coord Chem Rev 254:1179
- 2. Polshettiwar V, Varma RS (2010) Green Chem 12:743
- 3. Alonso F, Riente P, Yus M (2011) Acc Chem Res 44:379
- 4. Lee C-L, Syu C-M, Huang C-H, Chiou H-P, Chao Y-J, Yang C-C (2013) Appl Catal B 132:229
- 5. Lee C-L, Tsai Y-L, Chen C-W (2013) Electrochim Acta 104:185
- 6. Wang A, Yin H, Lu H, Xue J, Ren M, Jiang T (2009) Catal Commun 10:2060
- 7. Saxena A, Kumar A, Mozumdar S (2007) J Mol Catal A 269:35
- 8. Alonso F, Yus M (1996) Tetrahedron Lett 37:6925
- 9. Alonso F, Osante I, Yus M (2007) Tetrahedron 63:93
- Moglie Y, Alonso F, Vitale C, Yus M, Radivoy G (2006) Tetrahedron 62:2812
- 11. Alonso F, Radivoy G, Moglie Y (1999) Tetrahedron 55:4441
- 12. Radivoy G, Alonso F, Moglie Y (1999) Tetrahedron 55:14479
- 13. Alonso F, Riente P, Yus M (2008) Arkivoc 4:8
- 14. Alonso F, Riente P, Yus M (2008) Eur J Org Chem 29:4908
- 15. Alonso F, Riente P, Yus M (2008) Tetrahedron 64:1847
- 16. Alonso F, Riente P, Yus M (2008) Tetrahedron Lett 49:1939
- Dhakshinamoorty A, Pitchumani K (2008) Tetrahedron Lett 49:1818
- 18. Zank L, Zielinski J (2008) Appl Catal A 334:268
- Downing RS, Kunkeler PJ, Bekkum HV (1997) Catal Today 37:121
- 20. Saha A, Ranu B (2008) J Org Chem 73:6867
- 21. Corma A, Serna P (2006) Science 313:332
- 22. Sahiner N, Butun S, Ilgin P (2011) Coll Surf A 386:16

- 23. Freund PL, Spiro M (1985) J Phys Chem B 89:1074
- Valodkar M, Rathore PS, Jadeja RN, Thounaojam M, Devkar RV, Thakore S (2012) J Hazard Mater 201–202:244
- 25. Valodkar M, Modi S, Pal A, Thakore S (2011) Mater Res Bull 46:384
- Rathore PS, Advani J, Rathore S, Thakore S (2013) J Mol Catal A 377:129
- 27. Song P, Wen D, Guo ZX, Korakianitis T (2008) Phys Chem Chem Phys 10:5057
- 28. Huang X, Liao X, Shi B (2011) Green Chem 13:2801
- 29. Kojima Y, Haga T (2003) Int J Hydrogen Energy 28:989
- 30. Maas R, Chaudhari S (2005) Process Biochem 40:699
- 31. Walker GM, Weatherley LR (1999) Water Res 33:1895
- 32. Xu L, Wu X-C, Zhu J-J (2008) Nanotechnology 19:305603
- 33. Rezende TS, Andrade GRS, Barreto LS, CostaJr NB, Gimenez IF, Almeida LE (2010) Mater Lett 64:882
- 34. Alonso F, Radivoy G, Moglie Y (2000) Tetrahedron 56:8673
- Lebedeva VS, Vitukhnovskya AG, Yoshidac A, Kometanic N, Yonezawac Y (2008) Coll Surf A 326:204
- Pande S, Ghosh SK, Nath S, Praharaj S, Jana S, Panigrahi SJ (2006) Colloid Interface Sci 299:421
- 37. Kundu S, Ghosh SK, Mandal M, Pal T (2003) New J Chem 27:656
- Janaki V, Vijayaraghavan K, Oh B-T, Lee K-J, Muthucheli K, Ramasamy AK, Kamala-Kannan S (2012) Carbohydr Polym 90:1437
- 39. Yang W, Ma Y, Tang J, Yang X (2007) Colloid Surf A 302:628
- 40. Pal A, Shah S, Chakraborty D, Devi S (2008) Aust J Chem 61:833