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## PAPER

## A novel synthesis of highly stable palladium nanoparticles and their application in the reduction of nitroaromatic compounds

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Fuad Othman Abdullah<sup>1,2,\*</sup> , Leila Behrouzi<sup>3</sup> and Babak Kaboudin<sup>3,\*</sup> <sup>1</sup> Department of Chemistry, College of Science, Salahaddin University-Erbil, 44001, Kurdistan Region, Iraq<sup>2</sup> Department of Pharmacognosy, Faculty of Pharmacy, Tishk International University-Erbil 44001, Kurdistan Region, Iraq<sup>3</sup> Department of Chemistry, Institute for Advanced Studies in Basic Sciences (IASBS), Gava Zang, 45137-66731, Zanjan, Iran

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E-mail: [fuad.abdullah@su.edu.krd](mailto:fuad.abdullah@su.edu.krd) and [kaboudin@iasbs.ac.ir](mailto:kaboudin@iasbs.ac.ir)**Keywords:** phytochemicals, palladium nanoparticles, nitro aromatic compounds, reduction, aromatic aminesSupplementary material for this article is available [online](#)**Abstract**

Herein, a mild and efficient method for synthesis of highly stable palladium nanoparticles (PdNPs) on *Aristolochia Olivieri* (AO) extract as a support and reducing agent is described. Investigation of catalytic activity of obtained catalyst (AO@PdNPs) was performed for the reduction of nitroaromatic compounds. Of note are the functional group tolerance, fast rate, and the ability to apply a scope of nitro compounds (up to 30). The synthesized catalyst was characterized with UV–visible spectra, FE-SEM, EDS, XRD, AAS, FT-IR, and TEM techniques. The corresponding amine product was obtained excellent to high yields. The catalytic activity of AO@PdNPs for the hydrogenation of 4-methyl-2-nitroaniline and 4-methoxy-2-nitroaniline was pursued by UV-visible spectroscopy which presented excellent activity of catalyst.

**1. Introduction**

Aromatic amines are widely found in the structure of dyes, pharmaceuticals, and polymers [1–3]. The usual and simple method for the synthesis of aromatic amines is the selective reduction of nitro compound. The previously suggested reaction processes have reported at high temperature, intensive pressures, stoichiometric amount of reagents, costly ligands, and commercially [4]. In recent years, due to economic atoms issues and adaptability of environmental concerns, catalytic reduction of nitroaromatic compounds into aromatic amines has considered the attention of chemists [5, 6]. Following latest papers exhibited that metals have had an excellent activity for the reduction reactions especially in the nanoparticles forms (platinum, palladium, gold, cobalt, and iron) [7–11]. Palladium nanoparticles (PdNPs) have great chemical, physical and optical properties so, received more and more notice as a catalyst in chemical reactions. Traditional methods for the synthesis of PdNPs are chemical, sonochemical, and polyols reductions that used hazardous chemical materials [12]. However, the presentation of safe and environment-friendly ideas instead of toxic and dangerous existed methods is very remarkable [6, 13]. In the last decade, studies of biofabrication of metal nanoparticles have shown that the synthesis of palladium nanoparticles through a biocompatible is more effective than common chemical ways [14–16]. Despite its short history of rarely several decades, synthesis and stabilization of PdNPs utilizing biological sources is an emerging step in the green catalyst field. Several research groups have reported the palladium nanoparticles synthesis of biological resources. For example, Yun and co-workers developed a Phyto-crystallization of palladium applying *Cinnamomum zeylanicum* bark extract (CBE) [17]. Then the group of Roopan exhibited the PdNPs synthesis of *Annonasqamosa* extract [18]. Alternatively, a procedure based on the use of *Chlorella vulgaris* extract for the synthesis of palladium nanoparticles was also reported [19]. In addition, biologically synthesized PdNPs have been explained for different organic applications such as coupling reactions, alcohol oxidation, and reduction of nitroaromatic compounds [20–24].

*Aristolochia* plant is one of the well known natural products due to its widespread implementation traditionally uses. The *Aristolochia* plant extract contains a rich variety of phytochemicals such as aristolochic acids, flavonoids, alkaloids, and lignans [25]. Phytochemicals such as, phenolic, alkaloids, steroids, flavonoids, saponins, and terpenes have a vital role for the synthesis of nanoparticles via their reducing and capping ability to prevent their aggregation [14–19]. Herein, we demonstrated the highly stable method for the synthesis of PdNPs using *Aristolochia Olivieri* (AO) plant extract as a reducing and stabilizing agent. Moreover, the catalytic activity of synthesized AO@PdNPs explored for reduction of the variety of nitroaromatic compounds.

## 2. Experimental section

### 2.1. Chemicals

Chemical compounds such as, palladium(II) acetate, NaBH<sub>4</sub> and all of nitro compounds were purchased from Sigma-Aldrich (Steinheim, Germany) and deionized (DI) water was used in all experiments. The plant of *Aristolochia olivieri* was collected in April from Sakran Mountain, choman/ Kurdistan region of northern Iraq. The voucher specimens, accession number (7705) were deposited in the Herbarium at Salahaddin University-Erbil, Kurdistan-Iraq. The whole plants were air-dried separately under shade at room temp (20 °C–25 °C).

### 2.2. Preparation of extract and synthesis of catalyst

In order to generate the extract of *Aristolochia Olivieri* leaves, 12.5 g of *Aristolochia Olivieri* was added to 250 ml of deionized water in round-bottom flasks of 500 ml capacity. The mixture was stirred for 12 h at room temperature. The obtained extract was filtered with Premium Filter paper no.40. Then, 25 ml of  $0.7 \times 10^{-3}$  M aqueous palladium (II) acetate solution was added to 250 ml of extract at room temperature and the solution was stirred at reflux (100 °C) for 2 h under argon atmosphere.

The formation of catalyst was confirmed through observing the changing of reaction mixture color, which turned light brown to dark brown during this process. Furthermore, the synthesized catalyst was separated by centrifugation at 10000 rpm for 20 min, washed with ethanol ( $3 \times 25$  ml) and dried in an oven at 60 °C for 2 h.

### 2.3. Reduction of nitro-compounds

The general procedure including a laboratory flask was charged with a stir bar, the substrate (0.2 mmol), AO@PdNPs (5 mg, 0.011 mol%), and reductant agent (0.8 mmol). The solvent was added, and the resulting solution was allowed to stir for 2 h at room temperature. After completion of the reaction, the reaction mixture is transferred to a reparatory funnel, and ethyl acetate was added to a mixture of reaction. The organic layer was washed twice with H<sub>2</sub>O, dried with Na<sub>2</sub>SO<sub>4</sub>, and concentrated. The resulting products used for GC and TLC analysis.

## 3. Results and discussion

### 3.1. Synthesized and characterization of stable PdNPs

The stable PdNPs were prepared by adding of an aqueous solution of Pd(OAc)<sub>2</sub> to extract of *Aristolochia Olivieri* leaves. The formation of catalyst was confirmed through observing the changing of reaction mixture color from light brown to dark brown during the preparation. Atomic absorption spectroscopy (AAS) studies showed that the Pd content in the final catalyst was 0.1 mmol/g. The synthesized AO@PdNPs were characterized using several analytical techniques such as FE-SEM, XRD, FT-IR, TEM, UV-vis, AAS and EDS.

The morphology of the catalyst was studied by the Field Emission Scanning Electron Microscopy (FE-SEM) (figure 1). Figure 1 reveals PdNPs on the surface. Energy dispersive x-ray spectroscopy (EDS) (figure 2) presented from SEM analysis proved the presence of PdNPs in the structure of the catalyst. The results depicted spherical morphology with average size 32 nm.

The XRD analysis of the AO@PdNPs (figure 3) displayed Bragg's reflections related to Pd (0) at  $2\theta = 40.2$ , 46.7 and 68.2 related to (111), (200), (220) planes of face-centred cubic crystal (FCC) structure. The comparison of XRD analysis of AO@PdNPs and JCPDS card No 96-101-1111 confirmed the lattice constant.

Figure S1 (available online at [stacks.iop.org/MRX/8/095002/mmedia](https://stacks.iop.org/MRX/8/095002/mmedia)) shows FT-IR spectra of extract and the catalyst (AO@PdNPs). The significance absorption peaks appear at 3438, 2915, 1647, 1420 and 1044 cm<sup>-1</sup>. The strong absorption peak at 3438 cm<sup>-1</sup> was resulted from stretching of the O–H groups due to the presence of flavonoids, alcohols, phenols, and etc. The peaks were absorbed that 2915, 1647, 1420 and 1044 cm<sup>-1</sup> related to the stretching polyols, amide or C=C stretching of aromatic rings, C–O–C (esters, ethers) and C–OH/ C–H (polysaccharides), respectively. The absorption of palladium nanoparticles on the surface of the support may be done by the interaction of  $\pi$ -electrons when there are not any ligating agents [26]. The secondary metabolites

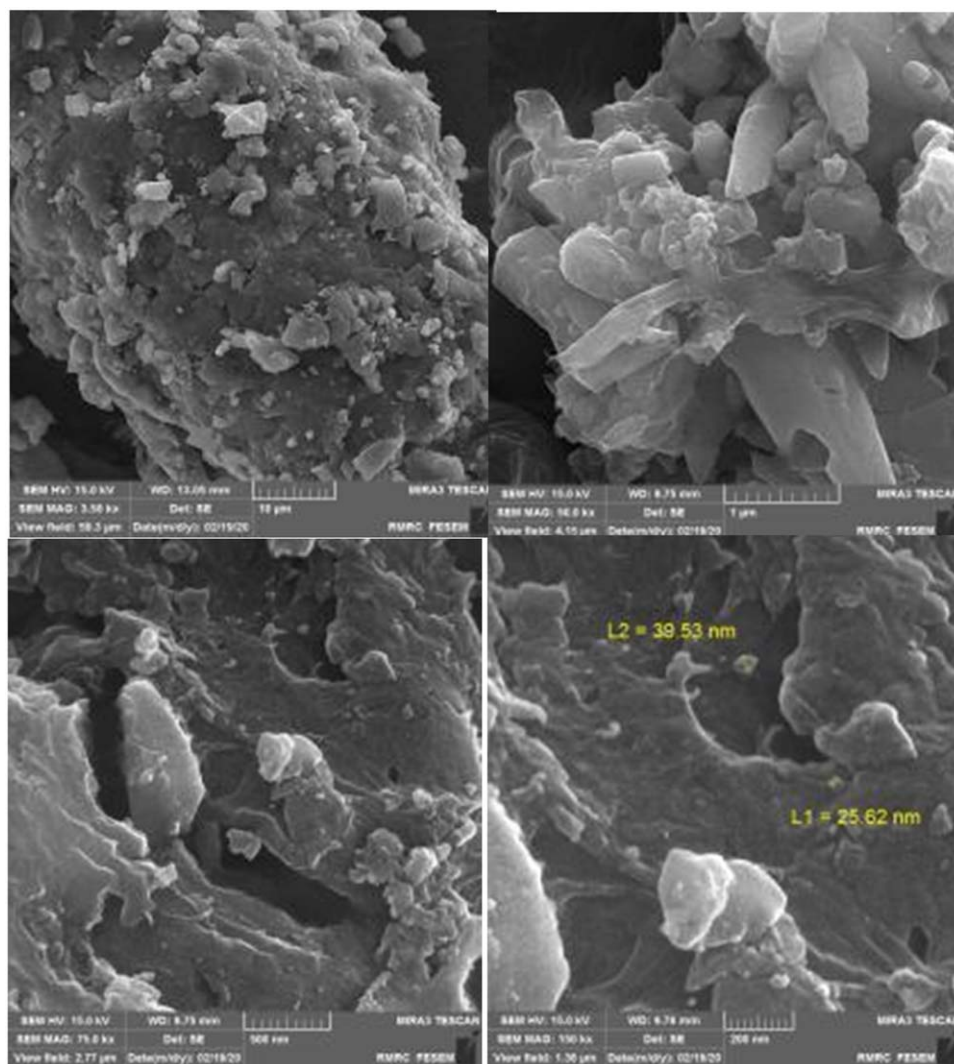


Figure 1. SEM analysis images of AO@PdNPs.

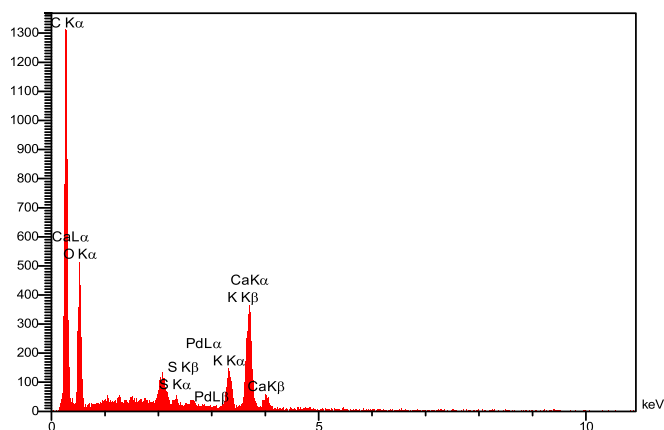


Figure 2. EDS spectrum of AO@PdNPs.

especially flavonoids and phenolic compounds in *Aristolochia olivieri* extract may have participated in the synthesis of palladium nanoparticles [27].

Transmission electron microscope (TEM) image of AO@PdNPs in different magnifications exhibited that the Pd nanoparticles are with spherical shaped on the surface of plant extract (figure 4).

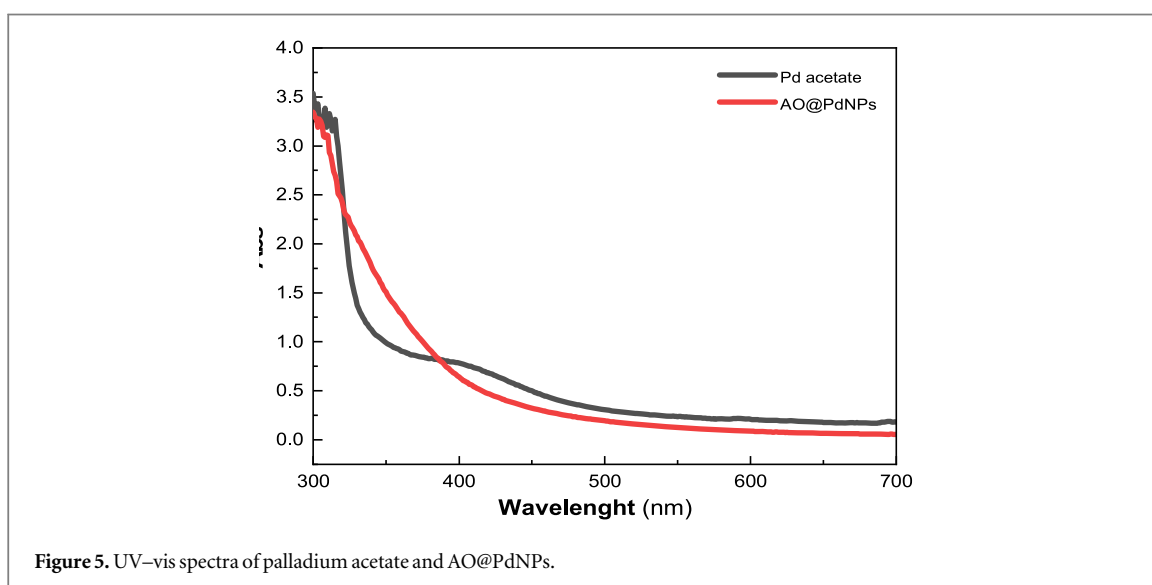
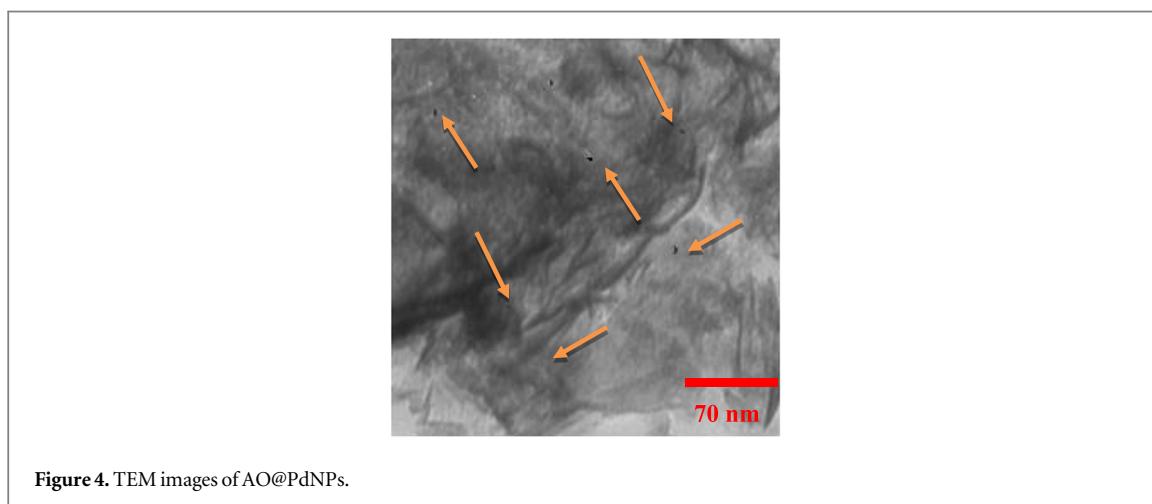
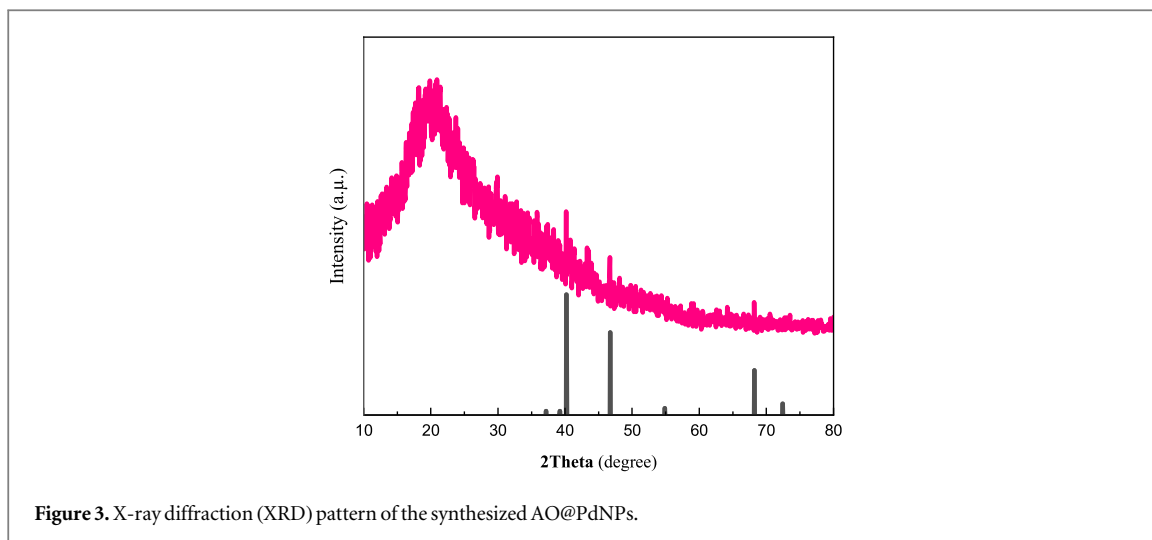
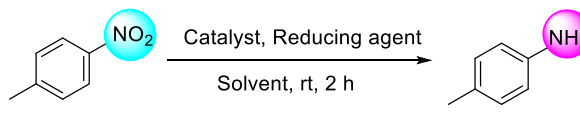


Figure 5 shows UV-vis spectra of palladium acetate and AO@PdNPs for comparison. The absorbance of the reaction was recorded from 300 to 700 nm. After the preparation of the catalyst, the absorption peak at 404 nm that attributed to Pd (II) ions was disappeared. The peak at 404 nm approved the preparation of the catalyst [28].

**Table 1.** Reaction conditions optimization for reduction of *p*-nitrotoluene.


Entry	Solvent	AO@PdNPs	Reductive (4.0 eq)	Yield <sup>a</sup> (%)
1	EtOH	0.011 mol%	NaBH <sub>4</sub>	2
2	DMSO	0.011 mol%	NaBH <sub>4</sub>	5
3	EtOAc	0.011 mol%	NaBH <sub>4</sub>	6
4	PEG	0.011 mol%	NaBH <sub>4</sub>	67
5	THF	0.011 mol%	NaBH <sub>4</sub>	NR
6	H <sub>2</sub> O	0.011 mol%	NaBH <sub>4</sub>	68
7	H <sub>2</sub> O:DMF <sup>b</sup>	0.011 mol%	NaBH <sub>4</sub>	38
8	H <sub>2</sub> O:EtOAc <sup>b</sup>	0.011 mol%	NaBH <sub>4</sub>	42
9	H <sub>2</sub> O:EtOH <sup>b</sup>	0.011 mol%	NaBH <sub>4</sub>	70
<b>10</b>	<b>H<sub>2</sub>O:THF<sup>c</sup></b>	<b>0.011 mol%</b>	<b>NaBH<sub>4</sub></b>	<b>100</b>
11	H <sub>2</sub> O:THF	0.011 mol%	HCO <sub>2</sub> NH <sub>4</sub>	trace
12	H <sub>2</sub> O:THF	0.011 mol%	NH <sub>2</sub> NH <sub>2</sub>	NR
13	H <sub>2</sub> O:THF	0.011 mol%	Glycerol	NR
14	H <sub>2</sub> O:THF	0.0066 mol%	NaBH <sub>4</sub>	70
15	H <sub>2</sub> O:THF	0.011 mol%	NaBH <sub>4</sub> (3 equiv)	15

<sup>a</sup> Yields determined by GC.

<sup>b</sup> 0.5 ml:0.5 ml,

<sup>c</sup> 0.8 ml:0.2 ml.

### 3.2. Nitro aromatic reduction

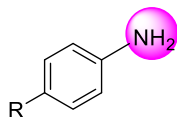
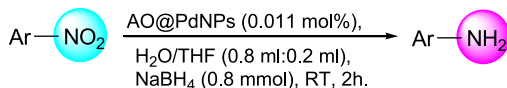
To check the efficiency of the synthesized and stabilized PdNPs with the flowers extract of *Aristolochia olivierias* as a catalyst for the reduction reactions, the reduction of 4-nitrotoluene was chosen as a model reaction and the effect of various factors such as reducing agent, solvent and amount of catalyst were examined (table 1). The reaction of 4-nitrotoluene (0.2 mmol) in ethanol with AO@PdNPs (5 mg, 0.011 mol%) and NaBH<sub>4</sub> (0.8 mmol) for 2 h at room temperature to give desired product in only 2% yield. A series of solvents were screened and the results showed that the reduction product was obtained in low to moderate yields (table 1, entries 1–6). The screening of various solvent showed that the water is relatively convenient solvent for this conversion. In further attempt to find appropriate condition, the reaction was examined in the mixture of solvents with water. The results of a mixture of organic solvents with water were shown in table 1 (entries 7–10). It was found that the reaction of 4-nitrotoluene in a solvent mixture of H<sub>2</sub>O:THF (8:2) in the presence of AO@PdNPs (5 mg, 0.011 mol%) and NaBH<sub>4</sub> (4 equiv) for 2 h at room temperature gave desired product in quantitatively yield (entry 10). The effect of other reducing agents was also examined and the results showed that the role of NaBH<sub>4</sub> is essential for the reduction reaction (table 1, entries 11–13). Decreasing the amount of pd nanoparticles to 0.0066 mol% caused a significant decline in yields (table 1, entries 14). Moreover, the poor conversion was observed when using a 3.0 equivalent of NaBH<sub>4</sub> (table 1, entry 15).

Under the optimized conditions, wide array nitroarenes were employed in the reduction reaction to corresponding amine in good to excellent yields. The obtained results are summarized in table 2. Reduction of different *ortho*, *para*, and *meta* substituted (electron withdrawing or donating groups) nitroarenes gave corresponding amine compound in good to excellent yields (entries 1–25). Sterically hindered *o*-nitroarenes gave the corresponding amines in moderate yields (entries 14–21 and 23). It is also possible to carry out this reduction process for nitronaphthalene (entry 24).

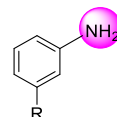
The reduction process of 4-nitrobenzenesulfonyl chloride, *trans*-4-methyl- $\beta$ -nitrostyrene, and 4-nitroisindoline-1,3-dione was failed to give corresponding amine compounds (entries 28–30).

Furthermore, the reduction of 1,4-dinitrobenzene was completed within 2 h to give *p*-phenylenediamine. The UV-visible analysis confirmed this conversion and the result showed that 1,4-dinitrobenzene effectively convert to *p*-phenylenediamine after 2 hours in 90% isolated yield (figure 6).

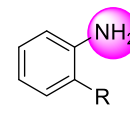
The main attention is focused in the recycling of the catalysts, especially in Pd catalysts, from the green chemistry point of view. The catalytic activity did not decrease considerably after three catalytic cycles (table 1S, see supporting information). The reaction yield dropped to ca. 38% at 4th recycling step.

**Table 2.** The reduction of several nitro compounds using AO@PdNPs as a catalyst.

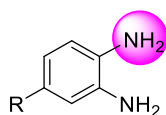
- 1.R=- H, 100% yield
- 2.R=- Me, 100% yield
- 3.R=- F, 100% yield
- 4.R=- Cl, 100% yield
- 5.R=- Br, 85% yield
- 6.R=- I, 86% yield
- 7.R=- OH, 100% yield
- 8.R=- OMe, 100% yield
- 9.R=- CH<sub>2</sub>OH, 95% yield



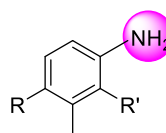
- 10.R=- Cl, 100% yield
- 11.R=- OH, 100% yield
- 12.R=- NH<sub>2</sub>, 100% yield
- 13.R=- CH<sub>2</sub>OH, 100 % yield



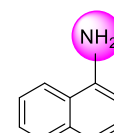
- 14.R=- Cl, 100% yield
- 15.R=- OH, 90% yield
- 16.R=- OMe, 70% yield
- 17.R=- Me, 80% yield
- 18.R=- CH<sub>2</sub>OH, 92% yield



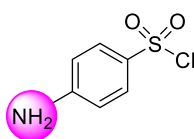
- 19.R=- Me, 80% yield
- 20.R=- OMe, 85% yield<sup>c</sup>
- 21.R=- Cl, 77% yield



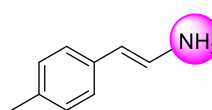
22. R = -Me, R'=-H, 70% yield<sup>b</sup>
23. R = -H, R'=-Me, 84% yield<sup>b</sup>



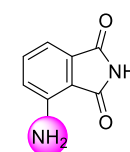
24. 90% yield<sup>b</sup>



25. ND<sup>b,d</sup>



26. ND<sup>b,d</sup>



27. ND<sup>b,d</sup>

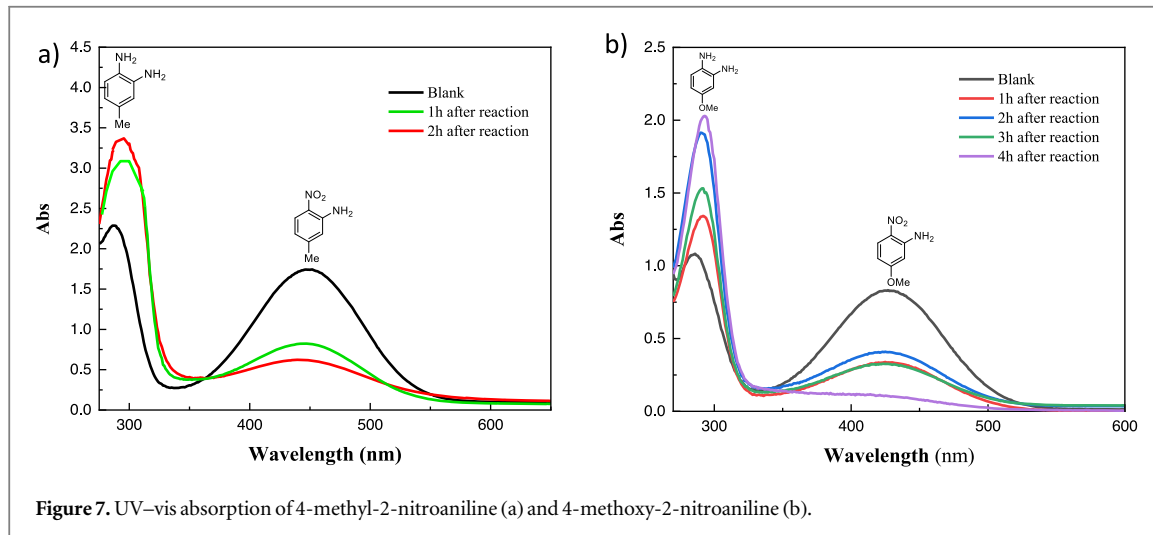
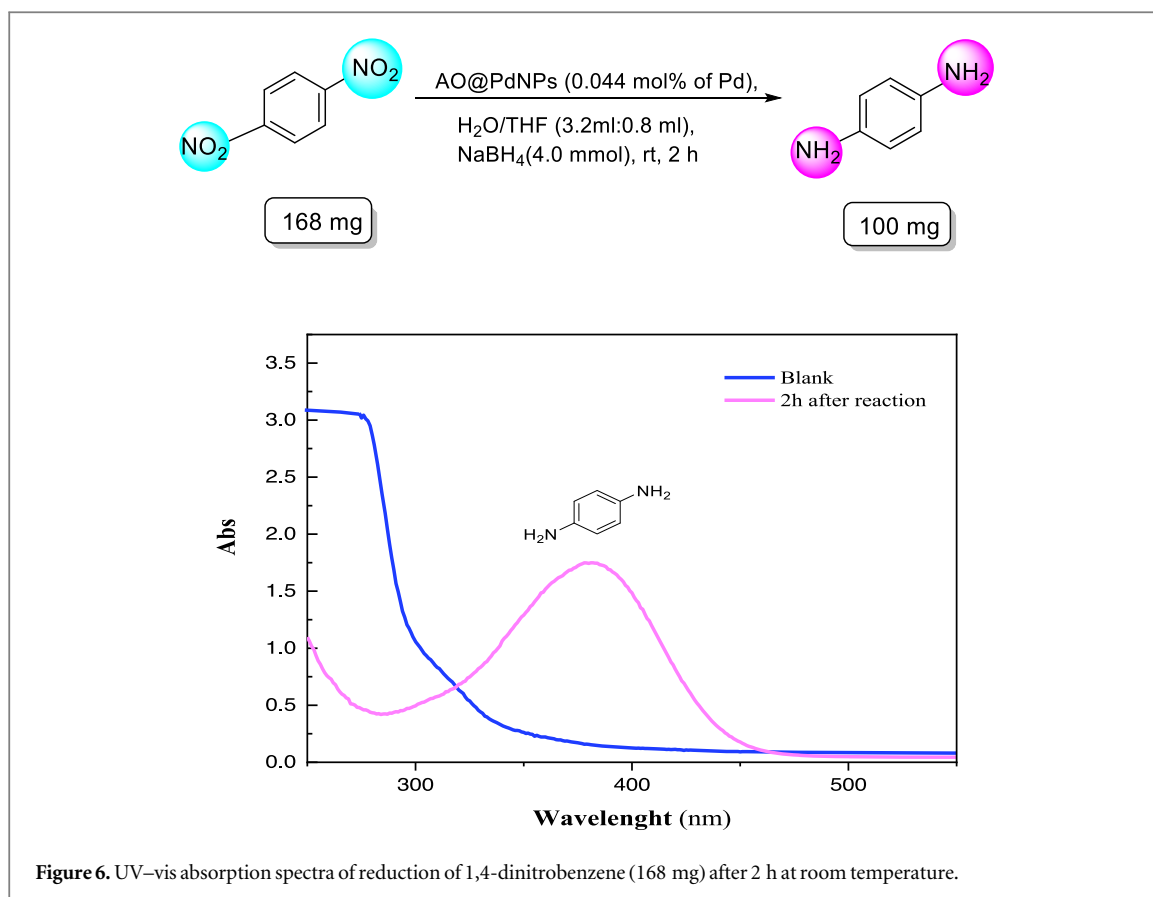
- <sup>a</sup> Yields determined by GC,  
<sup>b</sup> 0.022 mol% of catalyst,  
<sup>c</sup> Reaction completed at 4 h,  
<sup>d</sup> Reaction time is 12 h

In other attempt, the comparison of reduction process rate of 4-methyl-2-nitroaniline and 4-methoxy-2-nitroaniline was studied by UV-visible analysis. Results showed that the 4-methyl-2-nitroaniline was reduced with higher reaction rate than 4-methoxy-2-nitroaniline due to its higher stability by a resonance effect of methoxy group in para position (figure 7).

According to the literature [29], a proposed mechanism was outlined in Scheme 1. The reduction process of nitro aromatic compound was occurred via a hydride transfer from NaBH<sub>4</sub> to nitro group to yield a nitroso group, which subsequently reacted with more hydride to yield the amine compound (Scheme 1).

To get information about the stability and homogeneous or heterogeneous nature of the AO@PdNPs catalyst, a hot filtration test was carried out for the reduction of 4-nitrotoluene under optimized reaction conditions. The hot filtration test results exhibited that 4-nitrotoluene was converted to corresponding amine in 52% yield after 1 h. The reaction mixture was filtered and the filtrate allowed to react for more 2 h. Results showed that the corresponding amine was obtained in only 55% yield. This experiment revealed that the catalyst is stable and a heterogeneous reduction process carried out in the presence of AO@PdNPs.

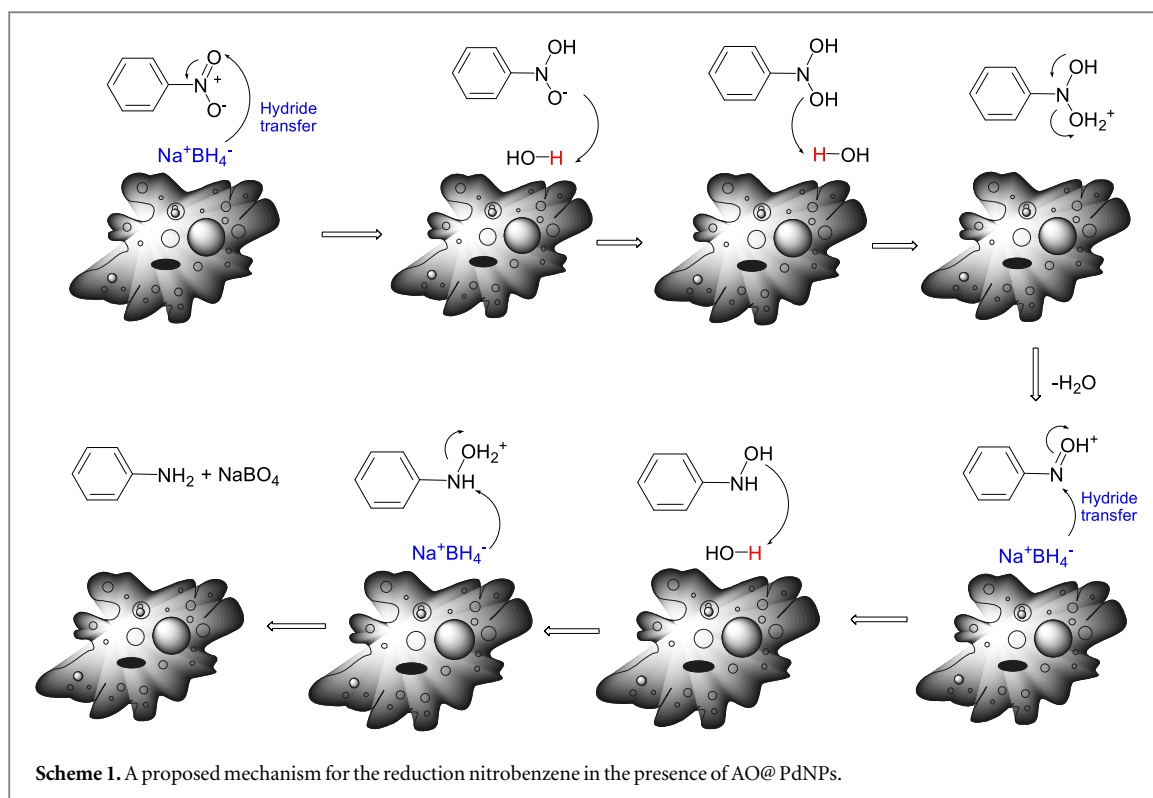
To the best of our knowledge, there are a few reports for the nitro reduction using PdNP supported on natural extract (table 3). The presented study provides advantages such as mild reaction conditions and applicable for the reduction of wide variety of nitro aromatic compounds.



#### 4. Conclusions

In summary, a biosynthesis procedure for the synthesis of palladium nanoparticles on *Aristolochia Olivieri* extract had exhibited. Reusing studies of AO@PdNPs for the reduction of the 4-nitrotoluene show that catalyst is recyclable for three-time and activity had decreased after the 4th run. Compared with previous reports, this method is much safe and eco-friendly because of uses less amount (0.011 mol %) of metal on natural support as well as the reaction completing under mild aqueous conditions. Furthermore, this process is suitable for a wide range of functional groups. The successful reduction of the 1 mmol scale is evident the potential of a new catalyst for use in large-scale reactions.





**Table 3.** A comparison of the results of the present system with the previous reports.

Conditions	yield
PhNO <sub>2</sub> , Pd/PEG4000, H <sub>2</sub> atmosphere, r.t., 3 h [11]	100%
PhNO <sub>2</sub> , polymer-anchored palladium (II) complex, H <sub>2</sub> atmosphere, DMF, 30 °C, 2.5 h [30].	99%
PhNO <sub>2</sub> , Pd NPs/RGO, NaBH <sub>4</sub> (2.0 mmol), EtOH:H <sub>2</sub> O (1:2), 50 °C, 1.5 h [31].	98%
ArNO <sub>2</sub> , AO@PdNPs (0.011 mol% of Pd), NaBH <sub>4</sub> (4.0 eq), H <sub>2</sub> O/THF (8: 2), RT, 2 h [This work].	100%

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## Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

## Conflicts of Interest

The authors declare no conflict of interest.

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