Bio-inspired synthesis of palladium nanoparticles fabricated magnetic Fe₃O₄ nanocomposite over *Fritillaria imperialis* flower extract as an efficient recyclable catalyst for the reduction of nitroarenes

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This current research is based on a bio-inspired procedure for the synthesis of biomolecule functionalized hybrid magnetic nanocomposite with the Fe₃O₄ NPs at core and Pd NPs at outer shell. The central idea was the initial modification of magnetic NP by the phytochemicals from *Fritillaria imperialis* flower extract, which was further exploited in the green reduction of Pd²⁺ ions into Pd NPs, in situ. The flower extract also acted as a capping agent for the obtained Pd/Fe₃O₄ composite without the need of additional toxic reagents. The as-synthesized Fe₃O₄@*Fritillaria*/Pd nanocomposite was methodically characterized over different physicochemical measures like FT-IR, ICP-AES, FESEM, EDX, TEM, XPS and VSM analysis. Thereafter, its catalytic potential was evaluated in the reduction of various nitrobenzenes to arylamines applying hydrazine hydrate as reductant in ethanol/water (1:2) medium under mild conditions. Furthermore, the nanocatalyst was retrieved using a bar magnet and recycled several times without considerable leaching or loss of activity. This green, bio-inspired ligand-free protocol has remarkable advantages like environmental friendliness, high yields, easy workup and reusability of the catalyst.

The catalytic society in recent days has shown significant interest and applied extensive thrust on the development of engineered heterogeneous catalysts as compared to their homogeneous analog. Their easy handling and facile isolation from the reaction mixture has made them advantageous¹-⁴. Among them, the magnetite nanoparticles (MNPs) have acquired remarkable attention as catalyst support or as the core of nanohybrid composites to serve as a potential reusable green catalyst⁵-⁷. The features like easy availability, abundance, small size thereby high surface area, excellent reactivity, high biocompatibility, good magnetic permeability, presence of plenteous hydroxyl groups for surface engineering and straightforward magnetic isolation has made them a fascinating material⁸-¹⁴. However, due to high surface energy, they are highly prone to self-aggregation which reduces their catalytic activity significantly¹⁵-¹⁸. This is somewhat minimized by surface functionalization. In recent years, the biogenic green approach for synthesis of NPs has come into prominence¹⁹-²⁴. Plants have been a ubiquitous and rich source in this regard. There are reports of using plant leaves, fruits, flowers, barks, and roots' extract as the cheap and abundant precursors of corresponding biomolecules for functionalization²⁵-³³. Following the trend of our earlier report towards the bio-inspired synthesis of stable and active nanocomposite catalysts³⁴-⁴⁰, we demonstrate herein the *Fritillaria imperialis* flower as bio-resource to fabricate Fe₃O₄ NP. The flower is grown widely in the plateau areas of Turkey, Iraq and Iran border and Himalaya foothills (Fig. 1). The
herb contains numerous phytochemicals including polyphenols, flavonoids, mild acids alkaloids and terpenoids. We further modified the biomolecule supported NPs by fabricating its exterior layer with tiny Pd NP as active catalytic phase. Finally, the catalytic application of the magnetic biogenic nanocomposite was demonstrated in the reduction of nitroarenes, a fundamental and significant chemical reaction in various organic transformations. Particularly, 4-nitrophenol is a detrimental organo-pollutant in water and dreadful for all living creatures. The reduced amines find wide applications in the synthesis of fine chemicals, agrochemicals, pharmaceuticals, dyes, polymers, pesticides, cosmetics and photography. In view of such consequences we designed our catalyst to carry out the reduction in a facile and green chemical pathway using hydrazine hydrate (N₂H₄·H₂O) as a mild and effective reductant. The magnetic core helps in efficient and effortless recoverability of the catalyst from the reaction mixture. Our protocol has been so proficient that a wide variety of nitro compounds has been converted to resultant amines within quick interval in aqueous ethanol producing outstanding yields and TOF.

Experimental

Synthesis of magnetite NPs. Following a typical co-precipitation method, a mixture of FeCl₂·4H₂O (2.0 g) and FeCl₃·6H₂O (5.2 g) were taken into deoxygenated water (25 mL) containing few drops of conc. HCl and subsequently, 250 mL of 1.5 M NaOH solution was added dropwise. The whole mixture was stirred vigorously at 60 °C. Immediately, brown colored Fe₃O₄ NPs were formed which were isolated using a magnetic stick. It was washed thrice with 200 mL deionized water and dried in air at 40 °C.

Preparations of Fe₃O₄@Fritillaria using the plant extract. 0.5 gm Fritillaria flower powder was extracted into 50 mL of Milli-Q water by swirling at 50 °C for 20 min. It was filtered over Whatman 1 paper and the filtrate was centrifuged at 4000 rpm for 5 min to precipitate out the impurities. The clear upper layer was preserved for the next step. For the preparation of Fe₃O₄@Fritillaria NPs, the magnetite NPs (0.5 g) were first dispersed in water by sonication for 20 min and the flower extract was added dropwise into it. The mixture was then stirred for 24 h at room temperature. Finally, the Fe₃O₄@Fritillaria nanocomposite was collected magnetically, washed thoroughly over DI-H₂O and dried in vacuum at 40 °C overnight.

Preparation of the Fe₃O₄@Fritillaria/Pd NPs. Five gram of the Fe₃O₄@Fritillaria NPs was dispersed over deionized water (100 mL) in sonicator for 20 min. An aqueous solution of Na₂PdCl₄ (40 mg in 20 mL H₂O) was poured into dispersion and refluxed for 12 h to assure the complete reduction of Pd(II) ions. The Fe₃O₄@Fritillaria/Pd nanocomposite was isolated as previous, rinsed with H₂O/acetone mixture to eliminate the adhered organic substances and dried likewise. The whole preparative schedule has been presented in Scheme 1. Pd content in the material was 0.08 mmol/g, analyzed by ICP-AES analysis.

Catalytic reduction of nitrobenzene. In a stirring solution of nitrobenzene (1 mmol) and Fe₃O₄@Fritillaria/Pd nanocomposite (0.1 mol% Pd, 13 mg) in H₂O/EtOH (2:1, 3 mL), the reducing agent NH₂NH₂·H₂O (3 mmol) was slowly dropped and the mixture was refluxed at 80 °C. After completion (by TLC, n-hexane/EtOAc: 5/2), EtOAc was added to the reaction mixture and stirred well. After removing the catalyst over a magnet, the water in reaction filtrate was soaked over anhydrous Na₂SO₄. Finally, the collected organic layer was concentrated to have pure aniline in 96% yield.

Results and discussion

Catalyst characterizations and data analysis. The current work illustrates an environmental friendly and green protocol involving Fritillaria flower extract to fabricate the ferrite MNPs surface and further to introduce stable Pd NPs. The biomolecules of Fritillaria flower has a significant tendency to accumulate over Fe₃O₄.
MNPs. The polyphenolic compounds of the flower extract contain hydroxyl and ketonic groups that chelate Pd\(^{2+}\) ions and subsequently reduce them green metrically (Scheme 1). The structural and physicochemical characteristics of the nanomaterial was characterized using diverse analytical techniques like FT-IR, ICP-AES, FE-SEM, TEM, EDX, XPS and VSM studies.

Figure 2 depicts comparative FT-IR spectra of bare Fe\(_3\)O\(_4\) NPs, Fritillaria extract, Fe\(_3\)O\(_4\)@Fritillaria and Fe\(_3\)O\(_4\)@Fritillaria/Pd nanocomposite in order to illustrate the stepwise synthesis. In the spectrum of Fe\(_3\)O\(_4\) NP (Fig. 2a), two broad peaks at 1622 and 3419 cm\(^{-1}\) correspond to the physisorbed H\(_2\)O and the surface OH groups. The characteristic peaks appeared at 584 and 439 cm\(^{-1}\) are due to the stretching and bending vibrations of Fe–O bond. Pure Fe\(_3\)O\(_4\) structure is characterized by a peak at 632 cm\(^{-1}\). Figure 2b represents the spectrum of Fritillaria extract which displays the significant peaks at 3385 cm\(^{-1}\) due to O–H groups of polyols\(^{49}\) and C-H stretching vibration from hydrocarbons and flavonoids at 2926 cm\(^{-1}\)\(^{50}\). Additionally, due to the presence of quinones, ketones, and carboxylic acids functions in the biomolecules contained in it, the distinctive peaks of C=O and O–C–O appears at 1709 cm\(^{-1}\) and 1072 cm\(^{-1}\) respectively\(^{51}\). An FT-IR band is observed in the range of 1400–1600 cm\(^{-1}\) owing to aromatic C=C stretching vibrations. The corresponding spectrum of Fe\(_3\)O\(_4\)@Fritillaria NPs is depicted in Fig. 2c. It is literally a combination of Fig. 2a,b indicating the successful functionalization of Fritillaria molecules over the ferrite NPs. These biomolecules actually perform as excellent capping agent, preventing the NPs from agglomeration and oxidation\(^{52}\). It also acts as reducing and stabilizing agent for immobilizing Pd NPs on the ferrite surface. The FT-IR spectrum of Fe\(_3\)O\(_4\)@Fritillaria/Pd NPs (Fig. 2d) is almost alike Fig. 2c except a small shift in C=O, C=C and O–H stretching frequencies. These shifts account for the attachment of Pd NPs on the surface modified MNPs.

The structural morphology, size and shape of the Fe\(_3\)O\(_4\), Fe\(_3\)O\(_4\)@Fritillaria, and Fe\(_3\)O\(_4\)@Fritillaria/Pd nanocomposite were investigated with the FE-SEM analysis as shown in Fig. 3. The materials are of nanometric size and of quasi-spherical shape (Fig. 3a). In addition, a continuous biopolymer layer is seen on the nanocomposite surface indicating the surface modification (Fig. 3a). The bright spots in Fig. 3c signifies the in situ synthesized Pd NPs being spread over the Fe\(_3\)O\(_4\)@Fritillaria composite. EDX analysis of the material was conducted in order to know the chemical composition. The spectrum obtained on recording of signals at random points of the catalyst surface showed the presence of Fe, Pd as...
metallic and C, O as non-metallic components. The non metals justify the attachment of phyto-compounds in the composite (Fig. 4).

In addition to the EDX analysis, elemental mapping of Fe3O4@Fritillaria/Pd nanocomposite also carried out to have the knowledge of component distributions over the catalyst surface. X-ray scanning of a segment of the FE-SEM image reveals the homomorphic dispersion of all the components on the nanocomposite (Fig. 5). The uniform distribution of the active site definitely has a significant role behind its catalytic superiority.

The TEM image of the Fe3O4@Fritillaria/Pd NPs exhibits that the Pd NPs are formed with almost globular morphology (Fig. 6). As can be seen in the image (Fig. 6a), the ferrite NPs are of 10–20 nm in dimension that are coated by thin layers of Fritillaria extract. The biomolecular layers from the extract acts as the green reducing
agent of the Pd ions as well as the stabilizing agent of Pd NPs. It easily detectable that the dark Pd NPs are of ~20–30 nm being entrapped in the modified iron oxide surface (Fig. 6b).

Figure 7 illustrates XRD patterns of Fe₃O₄ and Fe₃O₄@Fritillaria NPs. Evidently, XRD profile of the latter carries all the significant peaks that of cubic spinel Fe₃O₄ NPs. The XRD peaks found at 2θ = 30.3°, 35.7°, 43.4°, 53.9°, 57.4° and 62.9° can be attributed to diffraction on (220), (311), (400), (422), (511) and (440) planes respectively (JCPDS No. 19-0629). It also implies that the interior structure remains undisturbed even after bio-functionalizations and Pd anchoring. The Pd attachment can also be demonstrated by the distinctive peaks observed at 2θ = 40.1°, 46.6° and 67.9°, being ascribed to the (111), (200) and (220) crystalline planes of Pd fcc structure.

Magnetic characteristics of the Fe₃O₄@Fritillaria/Pd NPs was assessed through VSM analysis and the magnetization curve has been shown in Fig. 8. From the corresponding hysteresis curve, the maximal saturation

Figure 3. FE-SEM images of the (a) Fe₃O₄ NPs, (b) Fe₃O₄@Fritillaria NPs, (c) Fe₃O₄@Fritillaria/Pd NPs.
magnetization of Fe₃O₄@Fritillaria/Pd NPs was found to appear at 42.5 emu g⁻¹. However, the value is much lower than bare ferrite NP (64.2 emu g⁻¹) due to surface operations. Still, in the modified material the magnetization goes down from plateau state to zero on removal of the magnetic field which justifies it to be superparamagnetic.

Catalytic applications of Fe₃O₄@Fritillaria/Pd nanocomposite. So as to explore the catalytic application of Fe₃O₄@Fritillaria/Pd nanocomposite and finding optimum reaction conditions, we selected the reduction of nitrobenzene as a model reaction. The effect of various conditions including temperature, solvents, catalyst load, amount of reductant and time reaction were studied over the reaction. The outcomes were documented in Table 1. Primarily, the model reaction was examined in various solvents like dimethyl formamide (DMF), EtOH, MeOH, CH₃CN, H₂O/EtOH and H₂O. Among them, H₂O/EtOH afforded the best yield and thereby selected as the optimum solvent. The amount of Fe₃O₄@Fritillaria/Pd nanocomposite was also explored for the model reaction. Based on the study, 0.1 mol% catalyst was the most convenient for 1 mmol of nitrobenzene. Finally, the best result for the reduction of nitrobenzene was obtained using 3.0 mmol NH₂NH₂·H₂O as reductant and 0.013 g Fe₃O₄@Fritillaria (0.1 mol% Pd) catalyst respectively in H₂O/EtOH (2:1) solvent at 80 °C. We also performed the reduction of nitrobenzene using the bare Fe₃O₄@Fritillaria NPs but only a trace of aniline was obtained. This indicates that the interaction between the Pd NPs and Fe₃O₄@Fritillaria is very important for catalytic success.

After resolving the required optimizations, the next endeavor was to generalize them over a range of differently functionalized (electron-donating and electron-withdrawing groups) nitroarenes. The results in terms of reaction yield and TOF are shown in Table 2. All the reactions were executed superbly with all kind of substrates without noticeable influence of functional groups on the reaction. All the reactions were completed within 0.5–2 h.

Recyclability of Fe₃O₄@Fritillaria/Pd catalyst. For every heterogeneous catalytic system, the isolation and recycling of catalyst is a crucial feature in view of sustainable and industrial concern. The reusability of Fe₃O₄@Fritillaria/Pd was examined over the reduction of nitrobenzene under optimized conditions. After finishing a fresh batch of reaction the catalyst was recovered using a bar magnet and washed several times with ethanol and water. It was regenerated after drying at moderate temperature. To our delight, we could have reused it for eight consecutive cycles of reaction without noticeable loss in its activity (Fig. 9). We further analyzed the structural morphology of Fe₃O₄@Fritillaria/Pd nanocomposite after recycling 7 times by using TEM and EDX. As clearly can be seen from the TEM image (Fig. 10), the catalyst retains its initial morphology and particles size without any sign of agglomeration. Alongside, there occurs no change in elemental composition as evident from EDX data (Fig. 10), which in turn validates the robustness of our material.

Heterogeneity test for Fe₃O₄@Fritillaria/Pd catalyst. The Sheldon’s test was carried out to assure heterogeneous nature of the synthesized material, whether any Pd species leaked out in the filtrate solution. The reduction of nitrobenzene was continued over the catalyst under optimized state for 15 min and then the reaction mixture was divided into two-halves. From one portion of the reaction mixture the catalyst was removed by a magnetic bar and both the part reactions were further continued for another 15 min. On gas chromatographic analysis, it was revealed that no significant progress in reaction was achieved under non-catalytic conditions.
(60% conversion) while the other portion leaded to completion. The result is shown in Fig. 11. This further suggests that there was hardly any leaching of Pd NPs took place in the reaction mixture justifying its true heterogeneity.

Figure 5. Elemental mapping of Fe₃O₄@Fritillaria/Pd nanocomposite.
**Study of reaction mechanism.** Based on earlier published works, a probable reaction pathway has been documented in Scheme 249-57. The reaction goes through several intermediates. At the outset, hydrazine gets adsorbed on the surface of Pd NPs (I) which subsequently generates N₂ and nascent hydrogen by bond cleavage. This hydrogen is captured by the active Pd NPs to form metal hydride (II). In the meantime the substrate nitroarenes also get adsorbed over the catalyst surface and gets reduced by hydride transfer from II to form active nitroso derivative (III). This moiety is then further reduced to amine via hydroxylamine (IV) intermediate through hydrogen transfer. The hydrogenation of hydroxylamine is considered to be slow and rate determining step. Finally, the desired product leaves behind the catalyst surface to be used for the next cycle.

*Figure 6.* TEM images of (a) Fe₃O₄@Fritillaria NPs and (b) Fe₃O₄@Fritillaria/Pd NPs.
Uniqueness of our result. The individuality of our protocol was affirmed by comparing the catalytic performance between our methodology and the reported procedures in the reduction of 4-nitrophenol. The results are shown in Table 3 which evidently displays that the Fe₃O₄@Fritillaria/Pd nanocomposite is much superior to others in terms of reaction time and yield.

Conclusion
We introduce a facile procedure for the synthesis of a heterogeneous and reusable Pd NPs decorated on Fritillaria imperialis flower extract modified magnetic ferrite nanoparticles by post functionalization approach. Catalytic performance of the Fe₃O₄@Fritillaria/Pd nanocomposite material was studied in the competent reduction of nitroarenes without the use of any added base. The protocol worked proficiently using hydrazine hydrate as the reducing agent under eco-friendly conditions affording various aromatic amines with excellent yields. In addition, due to strong magnetic nature, the Fe₃O₄@Fritillaria/Pd nanocatalyst could be reused as much as eight cycles in the reduction process emphasizing its true heterogeneity. In view of the outstanding catalytic behavior, the engineered material is anticipated to be a versatile support to feed many other noble metals like Ag, Au, Cu etc. towards many catalytic transformations and might find an excellent exposure in chemical industry.
Table 1. Standardization of reaction conditions in the reduction of nitrobenzene over Fe₃O₄@Fritillaria/Pd nanocomposite. *Reaction conditions: nitrobenzene (1.0 mmol), solvent (3.0 mL), open air; bIsolated yield.

| Entry | Catalyst (mol%) | Solvent | N₂H₄·H₂O (mmol) | Condition | Time (h) | Yield (%)b |
|-------|----------------|---------|-----------------|-----------|---------|------------|
| 1     | –              | EtOH    | 3               | Reflux    | 24      | 0          |
| 2     | 0.1            | EtOH    | 3               | Reflux    | 2       | 75         |
| 3     | 0.1            | MeOH    | 3               | Reflux    | 2       | 70         |
| 4     | 0.1            | H₂O     | 3               | Reflux    | 6       | 60         |
| 5     | 0.1            | DMF     | 3               | Reflux    | 2       | 55         |
| 6     | 0.1            | CH₃CN   | 3               | Reflux    | 2       | 50         |
| 7     | 0.1            | H₂O/EtOH (1:1) | 3    | Reflux    | 1       | 90         |
| 8     | 0.1            | H₂O/EtOH (2:1) | 3    | Reflux    | 0.5     | 98         |
| 9     | 0.05           | H₂O/EtOH (2:1) | 3    | Reflux    | 1       | 85         |
| 10    | 0.1            | H₂O/EtOH (2:1) | 2.5  | Reflux    | 1       | 90         |
| 11    | 0.1            | H₂O/EtOH (2:1) | 3.5  | Reflux    | 0.5     | 98         |
| 12    | 0.1            | H₂O/EtOH (2:1) | 3    | r.t       | 2       | 45         |

Table 2. Reduction of aromatic nitroarenes catalyzed by Fe₃O₄@Fritillaria/Pd NPs. *Reaction conditions: Nitroarene (1.0 mmol), NH₂NH₂·H₂O (3.0 mmol), catalyst (0.1 mol%), EtOH:H₂O (1:2, 3.0 mL), 80 °C; bIsolated yields; cTurnover frequencies (TOF = (Yield/Time)/Amount of catalyst (mol)).

| Entry | RC₆H₄NO₂ | Time (h) | Yield (%)b | TOF (10⁻³) (s⁻¹)c |
|-------|----------|----------|------------|-------------------|
| 1     | H        | 0.5      | 98         | 544               |
| 2     | 4-OH     | 0.5      | 98         | 544               |
| 3     | 2-OH     | 1        | 92         | 256               |
| 4     | 4-NH₂    | 1        | 95         | 264               |
| 5     | 4-CH₃    | 0.5      | 96         | 533               |
| 6     | 4-OCH₃   | 0.5      | 95         | 528               |
| 7     | 4-CN     | 1        | 92         | 256               |
| 8     | 2-NH₂    | 2        | 88         | 122               |
| 9     | 4-CHO    | 1.5      | 85         | 157               |
| 10    | 4-Cl     | 1.5      | 80         | 148               |

Figure 9. Reusability of Fe₃O₄@Fritillaria/Pd catalyst for reduction of nitrobenzene.
Figure 10. TEM and EDX data for reused Fe₃O₄@Fritillaria/Pd catalyst after 7 runs.
Figure 11. Hot filtration and leaching test of Fe₃O₄@Fritillaria/Pd in the reduction of nitrobenzene.

Scheme 2. Reaction mechanism for the reduction of nitrobenzene over Fe₃O₄@Fritillaria/Pd catalyst.
### Table 3. Catalytic comparison in the reduction of 4-nitrophenol.

| Entry | Catalyst (mol%) | Conditions | Time (h) | Yield (%) | References |
|-------|-----------------|------------|----------|-----------|------------|
| 1     | Au/MTA          | NaBH₄, EtOH, RT | 3        | 90        |            |
| 2     | Fe₃O₄Ni MNPs    | Glycerol, KOH, 80 °C | 3.5      | 88        |            |
| 3     | Pd NPs/RGO      | NaBH₄, EtOH–H₂O, 50 °C | 1.5      | 97        |            |
| 4     | Fe–phenanthroline/Co | N₂H₄, H₂O, THF, 100 °C | 10       | 97        |            |
| 5     | Nickel–iron mixed oxide | N₂H₄, H₂O, propan-2-ol, Reflux | 1.75     | 93        |            |
| 6     | [Pt]@SiCₓ      | AcOH, H₂, RT    | 3        | 99        |            |
| 7     | Rh             | N₂H₄, EtOH, 80 °C | 2.5      | 94        |            |
| 8     | Rh–Fe₃O₄ nanocrystals | N₂H₄, EtOH, 80 °C | 1        | 99        |            |
| 9     | PdCu/graphene   | NaBH₄, EtOH–H₂O (1:2), 50 °C | 1.5      | 98        |            |
| 10    | Fe₃O₄@Fritillaria/Pd | N₂H₄, H₂O, EtOH–H₂O (1:2), 80 °C | 0.5     | 98        | This work |

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**Author contributions**

T.T., R.T., S.S., S.L., B.M. and S.H.: Visualization, Writing original draft, Formal analysis. H.V.: Funding acquisition, Methodology, Supervision. B.K.: Writing original draft, Formal analysis, Writing-review and editing.

**Competing interests**

The authors declare no competing interests.

**Additional information**

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