Reduction of 4-nitrophenol using green-fabricated metal nanoparticles

Yetzin Rodriguez Mejía and Naveen Kumar Reddy Bogireddy

Noble metal (silver (Ag), gold (Au), platinum (Pt), and palladium (Pd)) nanoparticles have gained increasing attention due to their importance in several research fields such as environmental and medical research. This review focuses on the basic perceptions of the green synthesis of metal nanoparticles and their supported-catalyst-based reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP). The mechanisms for the formation of these nanoparticles and the catalytic reduction of 4-NP are discussed. Furthermore, the parameters that need to be considered in the catalytic efficiency calculations and perspectives for future studies are also discussed.

1 Introduction

In recent years, one issue that has generated significant concern due to its adverse effects, mainly on human health, is the contamination of water (surface and groundwater), including the ocean. The principal cause of this event is the high amounts of toxic and refractory pollutants, mainly 4-nitrophenol (4-NP), which is widely used in the pharmaceutical and textile industries for the production of herbicides, insecticides, synthetic dyes, and paints, and as a corrosion inhibitor and pH indicator, among other applications.

Therefore, the reduction of 4-NP to 4-aminophenol (4-AP) has become a crucial issue, given that 4-AP is a compound with a lower degree of toxicity. Among the various 4-NP reduction reactions, the reaction with sodium borohydride (NaBH₄) as a reducing agent (H₂ source) in conjunction with metal catalysts, such as Pd, Ag, Pt, Cu, Au, and their assemblies on dendrimers, polymeric matrices, microgels, metal-immobilized silica-coated supports, and graphene oxide, has gained more attention due to its eco-friendly and straightforward reduction process. Furthermore, chemical and green methods are widely employed for the fabrication of nanomaterials as catalysts for the 4-NP reduction reaction in aqueous and semi-solid media. Pradhan et al. primarily introduced 4-NP reduction as a model reaction using Ag nanoparticles. The catalytic reduction reaction was real-time monitored via UV-visible spectroscopy by observing the decrease in the absorption band at 400 nm belonging to the 4-NP.

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nitrophenolate ion (intermediate product) and increase in the band at 300 nm related to 4-AP.\textsuperscript{24,25} Subsequently, many studies have been reported, but compared to other techniques, green-synthesized catalysts play a vital role in the 4-NP reduction reaction due to their biocompatibility, low toxicity, low cost, and easy preparation process. Also, several green reducing agents, such as ascorbic acid,\textsuperscript{24} formic acid,\textsuperscript{25} tetramethyl disiloxane,\textsuperscript{25} plant or seed extracts, and microorganisms,\textsuperscript{26} have been studied.\textsuperscript{19,27–29}

The purpose of this review is to present the scientific advances in the green synthesis of noble metal nanoparticles and their application in the reduction of 4-nitrophenol in aqueous media, clearly explaining the reaction mechanisms of both metal nanoparticle synthesis and 4-NP reduction.

The overall publication trend in the last two decades is presented in Fig. 1. During the first decade (2000 to 2010), only less than 200 articles were published annually. On the contrary, during the second decade (2011 to 2020), a significant increase (almost four-fold higher) in the number of annually published articles was observed. During the pandemic period, many articles were published, which can be explained by the growing recognition and importance of 4-NP.

1.1 History of 4-nitrophenol

The three-step procedure to synthesize paracetamol was first proposed by J. von Mering in 1893, which was advertised in 1953 considering that it safer than aspirin. The steps in synthesis of paracetamol are as follows: nitration of phenol \( \rightarrow \) conversion of nitro group \( (4\text{-NP}) \rightarrow \) amino group \( (4\text{-AP}) \) and acetyl amino group \( \rightarrow \) paracetamol (Fig. 2).

4-Nitrophenol is also called para-nitrophenol (p-nitrophenol) or 4-hydroxy nitrobenzene. It has a nitro group at the para position in a phenolic compound \( (i.e., \text{hydroxyl} \ (-\text{OH}) \text{ group attached to a carbon atom in a benzene ring}) \). In general, it is used in pharmaceutical drugs and insecticides. Moreover, 4-NP is an intermediate product in the production of acetaminophen (paracetamol) from phenol (as mentioned above). Human beings may be exposed to 4-NP by drinking polluted water.

2 Update on 4-nitrophenol reduction using green-synthesized metal nanoparticles

There are few reports on the reduction of 4-nitrophenol. Pengxiang \textit{et al.},\textsuperscript{21} Maryam \textit{et al.},\textsuperscript{23} and Muhammad \textit{et al.}\textsuperscript{25} mainly focused on the synthesis-dependent fabrication of AuNPs and their nanocatalyst assemblies to reduce nitrophenol. In this review, we focus on green-fabricated monometallic, bimetallic Ag, Au, Pt, and Pd NPs and their assembled structures to reduce 4-NP using NaBH\(_4\) as the model reaction.

3 Catalyst fabrication and characterization

3.1 Green synthesis-mediated metal nanoparticles as catalysts

The fabrication of nanoparticles (from different metals) \textit{via} green synthesis has achieved great importance due to the fact that it “reduces” the use and formation of toxic compounds.\textsuperscript{29,30} The use of biological materials such as bacteria, fungi, algae, and plant extracts (roots, leaves, fruits, flowers, and seeds)\textsuperscript{20–22} avoids the use of intermediate base groups, making it a cost-effective, accessible, eco-friendly, and biocompatible method compared to other synthesis methods \( (i.e., \text{chemical and physical})\).\textsuperscript{26,33} Plant extracts contain phytochemicals (polysols, terpenoids, polynaphenes, carboxylic acids, flavones, amides, \textit{etc.}) that are capable of bioreducing metal ions to metal NPs.\textsuperscript{32,34,35}

For the fabrication of NPs \textit{via} green synthesis, most studies report the extraction of the substrate from plant material, as shown in our previous study, where \textit{Coffea arabica} seed (CAS) powder was used as a green precursor, where 50 mL of distilled water was mixed with 0.6 g of CAS power at 85 °C.\textsuperscript{29} After this process, the extract was filtered and metallic salts were added. When the reducing agents from the CAS extract came in contact with the metal salts, a visual color change was observed (the color variation depends on the metal ions), revealing the formation of NPs.\textsuperscript{32,36}

However, the reaction conditions such as the type of feedstock (microorganisms, plant material, \textit{etc.}), temperature, pressure, pH, reaction time, reducing agent and metal ion concentration directly affect the chemical, physical, and optical characteristics (particle size, shape, and texture) of the nanoparticles.\textsuperscript{17–43} For example, pH plays an essential role in the synthesis of NPs, affecting their size, shape, and reaction rate. Moreover, these nanoparticles are used for various applications, such as antimicrobial agents \( (e.g., \text{AgNPs})\),\textsuperscript{44,45} cell imaging in cancer detection \( (e.g., \text{AuNPs})\),\textsuperscript{46} alternative energy generation \( (e.g., \text{AuNPs})\),\textsuperscript{47,48} remediation of oily sewage,\textsuperscript{49,50} sensors \( (e.g., \text{AgNPs})\),\textsuperscript{51,52} and moreover, as sustainable catalysts for environmental remediation \( (e.g., \text{AuNPs and AgNPs})\).\textsuperscript{28,53} Environmental

![Fig. 1 Schematic representing the history of publications from 2000–2022 (up to 8\textsuperscript{th} March) on 4-nitrophenol/p-nitrophenol from Web of Science search results.](image_url)
remediation has become important due to the negative impacts caused by pollution, as mentioned above. Water is one of the resources with the greatest impact due to the release of pollutants by industry and mining. Therefore, NPs obtained by green synthesis are an alternative for reducing toxic organic compounds (as mentioned in the Introduction). The possible mechanism for the formation of green-synthesized metal nanoparticles catalyst is still under debate. Various studies have reported that the green precursors act as multifunctional agents with both reducing and capping capabilities, but limited efforts have been made to explore their chemistry. Some research groups proposed a possible understanding based on HPLC and FTIR results.

3.2 Catalyst characterization

The catalytic activity of metal nanoparticles depends on several properties, such as their synergistic effect, particle size, quantum effects, and surface properties. These properties can be investigated using several traditional characterization techniques. Primarily, the reduction of 4-NP is monitored using the absorption spectrum obtained by UV-visible absorbance spectroscopy and to identify the electronic transition bands of metal nanoparticles. The particle size of metal nanoparticles plays a significant role in the removal of 4-nitrophenol. These particle size measurements have been achieved using dynamic light scattering-based particle size analyzers and high-resolution transmission electron microscopy. As is known, the surface charge and functional groups present on the catalyst can improve the adsorption of the organic pollutant, followed by the fast catalyst reduction of 4-NP, which have been obtained from zeta potential and Fourier transform infrared spectroscopy (FT-IR) studies, respectively.

4 Reduction of 4-nitrophenol using green-synthesized metal nanoparticles

4.1 Gold nanoparticles (AuNPs) as catalysts

Briefly, Xin Huang et al. fabricated gold nanoparticles (AuNPs) for the first time using plant tannins. The resultant AuNPs were supported on the porous γ-Al2O3, and the formation of multiple hydrogen bonds with γ-Al2O3 and self-cross-linking interactions among the stabilized AuNPs were observed. Further, the
fabricated Al2O3–AuNPs were used as a reusable catalyst to reduce 4-nitrophenol in aqueous medium. Initially, the Al2O3–AuNP catalyst was mixed with a 4-NP solution, which was bubbled with N2 to remove the dissolved O2 in the solution. Subsequently, NaBH4 was added to the mixture, which initiated the catalytic reduction, and the reduction of 4-NP was monitored by measuring the characteristic absorption peak of 4-NP at 400 nm. In addition, the porous Al2O3–AuNPs exhibited better reusability than the conventional Au–Al2O3 catalyst.

Daizy Philip’s group69 also proposed the fabrication of gold nanoparticles using an aqueous extract of fenugreek (Trigonella foenum-graecum) given that it is simple, efficient, economical, and nontoxic. The synthesized gold nanoparticles were characterized and tested for their size-dependent catalytic activity towards the reduction of 4-NP. The smaller nanoparticles showed faster activity.

Sanoë Chairam et al.70 reported the preparation of mung bean starch (MBS)-mediated gold nanoparticles (AuNPs) through a green synthesis method, which were found to be efficient and recyclable catalysts for the reduction of 4-NP in the presence of NaBH4.

Recently, Mustaffa Shamsuddin’s80 group presented the use of thioctic acid-functionalized SiO2-coated Fe3O4-supported P. macrocarpa fruit extract-mediated AuNPs as a reusable catalyst for the reduction of 4-nitrophenol under various conditions. The optimization of the 4-nitrophenol reduction process was studied using the Box–Behnken design. Under the optimal conditions, the percentage reduction of 4-nitrophenol was 92% after 1 h, and the catalyst also maintained highly stable catalytic activity after five successive cycles.

Several other groups employed fungal Aspergillus sp. WL,71 Citrus maxima (fruit),74 fungus Mariannaea sp. HJ,73 longan polysaccharides,76 aspartame,77 Jujube polysaccharides,79 Mimosops elengi (bark),80 Cotoneaster horizontalis leaves,81 catechin-capped,82 Konjac glucomannan,83 caffie acid,84 Coffea arabica seed,85 Hedysarum polysaccharides86 and Sterculia acuminata (fruit) as precursors to obtain AuNPs (as an unsupported catalyst) for the reduction of 4-NP. The AuNPs obtained by green synthesis used to reduce 4-NP and their respective characteristics and reaction conditions are presented in Table 1.

Table 1 AuNPs obtained by green synthesis used for the reduction of 4-NP with their respective characteristics and reaction conditions

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Size (nm)</th>
<th>Shape</th>
<th>Catalyst conc. (mM)</th>
<th>NaBH4 conc. (mLg L⁻¹)</th>
<th>4-NP conc. (mM)</th>
<th>Time (min)</th>
<th>Rate constant (Kapp × 10⁻³) s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Unsupported NPs</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fungal Aspergillus sp. WL71 (2017)</td>
<td>4-29</td>
<td>Spherical</td>
<td>114.72 mg L⁻¹</td>
<td>30</td>
<td>2</td>
<td>2-6</td>
<td>9.8-25⁵</td>
</tr>
<tr>
<td>Citrus maxima (fruit)74 (2016)</td>
<td>25.7</td>
<td>Rod and spherical</td>
<td>1 mM</td>
<td>NR</td>
<td>0.25</td>
<td>20</td>
<td>1.5⁶</td>
</tr>
<tr>
<td>Fungus Mariannaea sp. HJ73 (2017)</td>
<td>11.7</td>
<td>Spherical, hexagon, and irregular shapes</td>
<td>0.195 g L⁻¹</td>
<td>100</td>
<td>2</td>
<td>3.3</td>
<td>24.7</td>
</tr>
<tr>
<td>Longan polysaccharides76 (2020)</td>
<td>7.8-15.6</td>
<td>Spherical</td>
<td>1.416 μM</td>
<td>500</td>
<td>0.6</td>
<td>42</td>
<td>4.65</td>
</tr>
<tr>
<td>Aspartame77 (2015)</td>
<td>1.2-50</td>
<td>Spherical</td>
<td>1.0 mM</td>
<td>100</td>
<td>4.0</td>
<td>9</td>
<td>6.8⁶</td>
</tr>
<tr>
<td>Mushroom Pleurotus florio78 (2013)</td>
<td>5-16</td>
<td>Spherical</td>
<td>3.5 mg</td>
<td>15</td>
<td>2</td>
<td>30</td>
<td>1.9-33⁸</td>
</tr>
<tr>
<td>Jujube polysaccharides79 (2019)</td>
<td>8-13</td>
<td>Spherical and monodisperse</td>
<td>6.67 nM</td>
<td>NR</td>
<td>NR</td>
<td>18</td>
<td>1.17</td>
</tr>
<tr>
<td>Mimosa pudaica flower80 (2017)</td>
<td>~24</td>
<td>Spherical</td>
<td>0.25 mM</td>
<td>250</td>
<td>5</td>
<td>15</td>
<td>5.0⁹</td>
</tr>
<tr>
<td>Mimusops elengi (bark)81 (2016)</td>
<td>9-14</td>
<td>Spherical</td>
<td>0.42 mM</td>
<td>13-14</td>
<td>0.05</td>
<td>5-8</td>
<td>6.53-7.33</td>
</tr>
<tr>
<td>Cotoneaster horizontalis leaves82 (2017)</td>
<td>18</td>
<td>Spherical</td>
<td>1 mM</td>
<td>30</td>
<td>2</td>
<td>10</td>
<td>NR</td>
</tr>
<tr>
<td>Catechin-capped83 (2014)</td>
<td>16.6</td>
<td>Polydisperse</td>
<td>0.5 mM</td>
<td>5.5</td>
<td>0.15</td>
<td>8.6</td>
<td>1.5⁹</td>
</tr>
<tr>
<td>Konjac glucomannan (KGM)84 (2014)</td>
<td>12-31</td>
<td>Uniform spherical</td>
<td>10 mM</td>
<td>10</td>
<td>0.05</td>
<td>8.6</td>
<td>6.03</td>
</tr>
<tr>
<td>Caffeic acid (CA)85 (2017)</td>
<td>38.61</td>
<td>Spherical</td>
<td>0.2 mM</td>
<td>200</td>
<td>0.4</td>
<td>15</td>
<td>5.73</td>
</tr>
<tr>
<td>Coffea arabica seed86 (2018)</td>
<td>28</td>
<td>Spherical</td>
<td>10 mM</td>
<td>100</td>
<td>10</td>
<td>38</td>
<td>0.8⁸</td>
</tr>
<tr>
<td>Trigonella foenum-graecum87 (2012)</td>
<td>15-25</td>
<td>Spherical</td>
<td>1.3 × 10⁻⁴ M</td>
<td>250</td>
<td>0.25</td>
<td>7</td>
<td>NR</td>
</tr>
<tr>
<td>Hedysarum polysaccharides88 (HPS)87 (2021)</td>
<td>5-8</td>
<td>Spherical</td>
<td>20 μL of 10% (stock Au salt)</td>
<td>11.34 mg</td>
<td>0.6</td>
<td>7</td>
<td>NR</td>
</tr>
<tr>
<td>Sterculia acuminata (fruit)⁹⁰ (2015)</td>
<td>26.5</td>
<td>Spherical</td>
<td>5 mM</td>
<td>20</td>
<td>1</td>
<td>36</td>
<td>1.8⁹</td>
</tr>
</tbody>
</table>

| Supported NPs | | | | | | | |
| Mung bean starch-AuNPs⁹⁸ (2017) | 10 | Spherical | 20-100 mg | 0.1-0.9 g | 1 | 13 | 0.36⁶ |
| Al2O3-Bayberry tannin-AuNPs⁹⁹ (2011) | 4.63-5.08 | Spherical | 2.5 μM | 10 | 0.2 | 5 | NR |
| Phaleria macrocarpa (Scheff.) Boerl. (P. macrocarpa) AuNPs supported on -NH-SiO2-Fe3O4 nanoparticles⁹⁰ (2020) | 2.4 ± 0.7 | Spherical | 2 mg | 100 | 0.05 | 60 | NR |

* NR = not reported. * Denoted values were recalculated for uniformity in the corresponding units with respect to other reports.
4.2 Silver nanoparticles (AgNPs) as catalysts

Abilash et al.\(^a\) reported the use of Brevnia rhamnoides stem extract-mediated spherical AgNPs to reduce 4-NP. The synthesized AgNPs exhibited relatively lower catalytic rates than Au NPs due to their relatively large size and the formation of a surface oxide layer. Further, Natarajan Sakthivel’s group\(^a\) reported the preparation of AgNPs using a fungus (Cylindrocladium floridanum), which were tested for the reduction of 4-NP as a homogeneous catalyst.

The reduction reaction rate was dependent on the reaction conditions such as concentration, size, and number of surface atoms of the catalyst. Later, Muniyappan et al.\(^a\) fabricated silver nanoparticles using Dalbergia spinosa leaves and tested them to reduce 4-nitrophenol. In addition to absorbance studies, they used \(^1\)H NMR spectroscopy to confirm the reduction of 4-nitrophenol and the formation of 4-aminophenol.

Recently, several other groups also devoted their efforts to the reduction of 4-nitrophenol using green-fabricated silver nanoparticles, such as Psidium guajava leaves,\(^b\) Tulsi leaves,\(^b\) pestle curcumin,\(^b\) seaweed Fucus gardneri,\(^b\) and others.\(^b\) The green-fabricated AgNPs used as catalysts to reduce 4-NP and their respective characteristics and reaction conditions are shown in Table 2.

### 4.3 Platinum and palladium nanoparticles as catalysts

In addition to Ag and Au nanoparticles, Pt and Pd NPs have been tested to reduce 4-NP to 4-AP with a similar mechanism understanding to that of Au and AgNPs. However, there are less reports on green-fabricated Pt and Pd NP-based 4-NP reduction probes than Ag and Au NPs. Generally, Pd and Pt NPs are among the most efficient catalysts for various organic reactions with fast reaction rates, high turnover frequency, and high yields.

#### Table 2  AgNPs obtained by green synthesis used for the reduction of 4-NP and their respective characteristics and reaction conditions\(^a\)

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Size [nm]</th>
<th>Shape</th>
<th>Catalyst conc. (mM)</th>
<th>NaBH₄ conc. (mM)</th>
<th>4-NP conc. (mM)</th>
<th>Time (min)</th>
<th>Rate constant (K_{app} \times 10^{-3} \text{ s}^{-1})</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Unsupported NPs</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Psidium guajava leaf (2019)</td>
<td>20–30</td>
<td>Polydisperse</td>
<td>10 µL</td>
<td>100</td>
<td>10</td>
<td>8</td>
<td>2.6(^b)</td>
<td>93</td>
</tr>
<tr>
<td>Fungus Cylindrocladium floridanum (2013)</td>
<td>25</td>
<td>Quasi spherical</td>
<td>4.63–27.81 (\times 10^{-4}) M</td>
<td>6.67</td>
<td>0.1</td>
<td>60</td>
<td>1.3(^b)</td>
<td>92</td>
</tr>
<tr>
<td>Tulsi leaves (2018)</td>
<td>5–10</td>
<td>Globular</td>
<td>10 µL</td>
<td>200</td>
<td>5</td>
<td>30</td>
<td>34.1(^b)</td>
<td>94</td>
</tr>
<tr>
<td>Dalbergia spinosa leaves (2014)</td>
<td>18</td>
<td>Quasi spherical</td>
<td>200 µL</td>
<td>0.1</td>
<td>0.1</td>
<td>NR</td>
<td>NR</td>
<td>95</td>
</tr>
<tr>
<td>Thymbra spicata leaves (2018)</td>
<td>7</td>
<td>Spherical</td>
<td>2 mg</td>
<td>250</td>
<td>2</td>
<td>60</td>
<td>64.5(^b)</td>
<td>96</td>
</tr>
<tr>
<td>Polyphenol (2019)</td>
<td>2–10</td>
<td>R</td>
<td>0.2 mg L(^{-1})</td>
<td>10</td>
<td>0.1</td>
<td>16</td>
<td>2.8(^b)</td>
<td>97</td>
</tr>
<tr>
<td>Salmalia malabarica gum (2016)</td>
<td>7</td>
<td>Spherical</td>
<td>10 µL</td>
<td>15</td>
<td>0.2</td>
<td>60</td>
<td>0.9(^b)</td>
<td>98</td>
</tr>
<tr>
<td>Kollicoat-capped Ag NPs (2016)</td>
<td>~20</td>
<td>Spherical</td>
<td>20 µL</td>
<td>100</td>
<td>0.1</td>
<td>60</td>
<td>NR</td>
<td>99</td>
</tr>
<tr>
<td>Leaf extract of Peronema canescens (2021)</td>
<td>19</td>
<td>Spherical</td>
<td>150 µL</td>
<td>30</td>
<td>2</td>
<td>30</td>
<td>NR</td>
<td>100</td>
</tr>
<tr>
<td>Extract of Brevnia rhamnoides (2011)</td>
<td>27</td>
<td>Spherical, rods, and hexagonal</td>
<td>0.3 mL</td>
<td>30</td>
<td>2</td>
<td>~7</td>
<td>9.19</td>
<td>91</td>
</tr>
<tr>
<td>Sterculia acuminata fruit (2016)</td>
<td>10–50</td>
<td>Spherical</td>
<td>10–100 µg mL(^{-1})</td>
<td>0.1 N</td>
<td>(10^{-4}) N</td>
<td>22</td>
<td>0.95(^b)</td>
<td>68</td>
</tr>
<tr>
<td>Simalia tuberosa Lour (2018)</td>
<td>25</td>
<td>Spherical</td>
<td>20 µL</td>
<td>1 mg</td>
<td>1</td>
<td>2880</td>
<td>NR</td>
<td>102</td>
</tr>
<tr>
<td>Seaweed Fucus gardneri (2018)</td>
<td>19.39</td>
<td>Quasi spherical</td>
<td>1 mg mL(^{-1})</td>
<td>0.03</td>
<td>2</td>
<td>5</td>
<td>9.3(^b)</td>
<td>103</td>
</tr>
<tr>
<td><strong>Supported NPs</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Herbal tea from Stachys lavandulifolia (Fe₃O₄@Si) (2018)</td>
<td>20–40</td>
<td>Quasi spherical</td>
<td>2 mg of catalyst (0.008 mol%)</td>
<td>0.3</td>
<td>3</td>
<td>0.5</td>
<td>63.4(^b)</td>
<td>104</td>
</tr>
<tr>
<td>AgNPs decorated with hydroxyapatite (2018)</td>
<td>14.79</td>
<td>Rod</td>
<td>2 mg</td>
<td>200</td>
<td>100</td>
<td>9</td>
<td>2.0–7.3</td>
<td>105</td>
</tr>
<tr>
<td>AgNPs decorated with SnO₂ microsphere (2017)</td>
<td>5</td>
<td>Spherical</td>
<td>1.5 mg</td>
<td>1.5 mg</td>
<td>20 mg L(^{-1})</td>
<td>300–2160</td>
<td>4.7–51.7(^b)</td>
<td>106</td>
</tr>
<tr>
<td>AgNPs synthesized with polyphenols and supported on modified graphene (Ag-TPG) (2015)</td>
<td>5</td>
<td>Spherical</td>
<td>0.5 mg mL(^{-1})</td>
<td>10</td>
<td>0.1</td>
<td>13</td>
<td>3.35</td>
<td>107</td>
</tr>
<tr>
<td>AgNPs supported on cellulose nanocrystals (CNC@PDA-Ag) (2015)</td>
<td>~10 nm</td>
<td>R</td>
<td>20 µg mL(^{-1})</td>
<td>38</td>
<td>0.12</td>
<td>18</td>
<td>0.76(^b)</td>
<td>108</td>
</tr>
<tr>
<td>AgNP-decorated halloysite nanotubes using dopamine (2018)</td>
<td>10–20</td>
<td>Rod</td>
<td>1 g</td>
<td>200</td>
<td>1</td>
<td>7</td>
<td>4.45(^b)</td>
<td>109</td>
</tr>
</tbody>
</table>

\(^a\) NR = not reported. \(^b\) Denoted values were recalculated for uniformity in the corresponding units with respect to other reports.
However, the metal aggregation and precipitation result in catalyst decomposition and considerable loss in catalytic activity. Therefore, from the viewpoint of practical application, the use of green-fabricated Pd and Pt NP probes is desirable, similar to Au and Ag NPs.

When stable and uniform-sized Pd and Pt NPs are fabricated, they possess tremendous catalytic efficiency for the conversion of 4-nitrophenol to 4-aminophenol, better than other metal nanoparticles. In addition, our group found that self-assembled PtNPs demonstrated significant catalytic efficiency for the reduction of 4-NP. The rate constant of *Coffeea arabica* seed-mediated self-assembled Pt nanoparticles (60 × 10⁻³ s⁻¹) was almost two-times higher than that of mushroom *Pleurotus florida*‐mediated AuNPs,⁷⁸ where due to the presence of sharp edges in their corners, the number of active surface sites in the anisotropic PtNPs is very high compared with bare NPs, and the small molecules from biomass could readily adsorb on the Pt surface.

For instance, even with only 5–50 µg of *Sterculia acuminata* mediated PtNPs,⁷⁷ the rate constant obtained was 3.0 × 10⁻³ s⁻¹. The superior catalytic activity of Pd and Pt NPs than that of equivalent Au and Ag NPs may be attributed to several other properties, such as their particle size and electron structure on the surface of their atoms (encourages the temporary sticking of molecules). The overall electron cloud changes shape, allowing the stuck molecules to rearrange into new compounds; however, catalyst does not change. Subsequently, the rearranged molecules are eventually pushed out by new input ones (temperature-caused motion).

Several other green precursors such as guar gum,⁶⁹ sodium rhodizionate,⁷¹ *Maytenus royleanus*,¹¹² *Sterculia Acuminata* fruit extract,⁶⁸ *Equisetum arvense* L/walnut shell,¹¹³ and *Silybum marianum*¹¹⁴ have been used to obtain Pt and PdNPs (as unsupported catalysts) for the reduction of 4-NP. Still, there is room to develop supported catalysts using Pt/Pd NPs for the reduction of 4-NP. Table 3 shows the Pt and PdNPs obtained by green synthesis used to reduce 4-NP and their respective characteristics and reaction conditions.

### 4.4 Bimetallic nanoparticles as catalysts

As is well known, the reduction of 4-nitrophenol using metal nanoparticles is mainly dependent on the size and shape of the NPs, and thus nanoengineering plays a crucial role in tailoring catalysts. Consequently, the presence of two or more metals in a single catalyst may increase the number of active sites in bimetal catalysts than single-metal catalysts. Also, there is the possibility of the synergistic effect in bimetal catalysts.¹¹⁵⁻¹¹⁷

In 2013, Bihua Xia et al.¹¹⁵ presented green-fabricated spherical Au/Ag bimetallic nanoparticles using degraded *Pueraria mirifica* starch as both a reduction and stabilizing agent. Further, the authors tested the catalytic efficiency of the fabricated bimetallic Au/Ag nanoparticles towards the reduction of 4-nitrophenol. Interestingly, the Au/Ag bimetallic nanoparticles exhibited rapid 4-NP reduction reaction catalytic efficiency compared to the bare Ag and Au NPs. The reaction time for the Au/Ag bimetallic nanoparticles was almost 14-times higher than that for the mono metal NPs fabricated using the same degraded *Pueraria mirifica* starch. Similarly, the Daizy Philip group¹¹⁶ reported the preparation of pomegranate fruit juice-mediated core–shell Au–Ag NPs and their use as catalysts for the reduction of 4-NP. They also obtained better catalytic efficiency with core–shell Au–Ag NPs than their monometallic NPs. The obtained apparent rate constant (13.3 × 10⁻³ s⁻¹) of the core–shell Au–Ag nanoparticles was higher than that of the unsupported bimetal catalysts presented in the table.

The superior catalytic efficiency of bimetallic NPs may be due to the existence of two metals (Au and Ag) in their composition and their morphological changes, where due to their synergistic effect.

**Table 3** Platinum and palladium NPs obtained by green synthesis used for the reduction of 4-NP and their respective characteristics and reaction conditions

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Metal</th>
<th>Size (nm)</th>
<th>Shape</th>
<th>Catalyst conc.</th>
<th>NaBH₄ conc. (mM)</th>
<th>4-NP conc. (mM)</th>
<th>Time (min)</th>
<th>Rate constant (K&lt;sub&gt;app&lt;/sub&gt; × 10⁻³ s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Platinum nanoparticles (PtNPs)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Guar gum (2014)</td>
<td>Pt</td>
<td>~6</td>
<td>Spherical</td>
<td>2.5 mM</td>
<td>100</td>
<td>1</td>
<td>240</td>
<td>7</td>
</tr>
<tr>
<td>Sodium rhodizonate (2018)</td>
<td>Pt</td>
<td>26</td>
<td>Spherical</td>
<td>50 µL</td>
<td>5 mg in 0.5 mL of water</td>
<td>0.2</td>
<td>10</td>
<td>18.1&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td><em>Maytenus royleanus</em> (2017)</td>
<td>Pt</td>
<td>5–8</td>
<td>Spherical</td>
<td>5 mg</td>
<td>20</td>
<td>1</td>
<td>20</td>
<td>2.1&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td><em>Sterculia Acuminata</em> fruit extract (2018)</td>
<td>Pt</td>
<td>~3.4</td>
<td>Spherical</td>
<td>10–100 µL</td>
<td>100</td>
<td>2</td>
<td>8</td>
<td>0.1&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td><em>Coffeea Arabica</em> seed (2021)</td>
<td>Pt</td>
<td>2</td>
<td>Spherical</td>
<td>10 µL</td>
<td>0.76 mg</td>
<td>1</td>
<td>3–5</td>
<td>60</td>
</tr>
<tr>
<td><strong>Palladium nanoparticles (PdNPs)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Equisetum arvense</em> L/walnut shell (2017)</td>
<td>Pd</td>
<td>5–12</td>
<td>Spherical</td>
<td>5 mg</td>
<td>250</td>
<td>2.5</td>
<td>1</td>
<td>NR</td>
</tr>
<tr>
<td><em>Sterculia acuminata</em> (2018)</td>
<td>Pd</td>
<td>~26.5</td>
<td>Spherical</td>
<td>5–50 µg</td>
<td>100</td>
<td>2</td>
<td>20</td>
<td>3.0</td>
</tr>
<tr>
<td><em>Silybum marianum</em> (2017)</td>
<td>Pd</td>
<td>&lt;20</td>
<td>Spherical</td>
<td>0.5 mL</td>
<td>15</td>
<td>20</td>
<td>27</td>
<td>NR</td>
</tr>
</tbody>
</table>

<sup>a NR = Not Reported. b Denoted values were recalculated for uniformity in the corresponding units with respect to other reports.</sup>
effect, electrons can transfer from one metal to the other metal NPs (i.e., the ionization potential of Au/Ag is 9.22/7.58 eV, respectively). This is important to enhance the electron cloud on the bimetallic NP surface in a kinetically favorable manner with more active sites. Table 4 demonstrates the bimetallic nanoparticles obtained by green synthesis to reduce 4-NP and their characteristics and reaction conditions.

Yinan Wang et al. fabricated a template (i.e., lipid as a tube-like template) based on palladium–platinum nanotubes using ascorbic acid. The fabricated Pd–Pt nanotubes (15 µg) showed an improved catalytic activity for the reduction of 4-NP. The calculated apparent rate constant (8.3 × 10⁻³ s⁻¹) of Pd–Pt NTs was almost 2.5-times higher than that of the Pt NTs (3.3 × 10⁻³ s⁻¹) presented in the same report. Furthermore, the fabricated Pd–Pt NTs were also tested for their recyclability over six cycles, and the authors did not observe any loss in their activity. Similar to the above-mentioned reports, the better catalytic efficiency of the PdPt NTs than Pt NTs is ascribed to the electron transfer effect.

Recently, Ye et al. synthesized lichen-reduced graphene oxide (LrGO)-AgAu composites using Cetraria islandica (L.) Ach. Extract. The fabricated LrGO–AgAu nanocomposites were examined for the reduction of 4-NP. Similar to previous reports on bimetallic NPs, higher catalytic activity was observed for the reduction of 4-NP than that with the monometallic nanoparticles related to the preparation of small-sized homogeneous particles, which give a significant amount of active sites on the nanocomposite surface.

The superior catalytic activity of bimetallic nanoparticles than that of monometallic nanoparticles may be attributed to several other properties, such as the synergic effect, particle size, quantum effects, and surface properties of the metal nanoparticles. Alternatively, rapid and easy procedures are essential to improve the reusability of catalytic probes.

### 4.5 Suggested studies during the 4-nitrophenol reduction process

#### 4.5.1 Effect of NaBH₄ concentration on 4-nitrophenol reduction

According to Fig. 2, NaBH₄ plays a vital role in the reduction of 4-NP. However, besides the rigorous reaction, at higher concentration, it leads to toxicity due to the presence of boron. Even though numerous studies employed higher concentrations of NaBH₄ than 4-NP to achieve a higher reaction rate and get a perfect fit in the pseudo-first-order reaction plot during the process, it is time to think about the Environmental Protection Agency (EPA)/World Health Organization (WHO) toxicity limit of boron, which is supposed to be under 2.4 µg

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Metal</th>
<th>Size (nm)</th>
<th>Shape</th>
<th>Reactant conc.</th>
<th>NaBH₄ conc. (mM)</th>
<th>4-NP conc. (mM)</th>
<th>Time (min)</th>
<th>Rate constant × 10⁻³ s⁻¹</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Unsupported NPs</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ascorbic acid (2019)</td>
<td>Pd–Pt</td>
<td>~57</td>
<td>Nanotubes</td>
<td>15 µg</td>
<td>100</td>
<td>0.009</td>
<td>10</td>
<td>3.4²</td>
<td>117</td>
</tr>
<tr>
<td>Morgenella psychrotolerans</td>
<td>Pd–Pt</td>
<td>NR</td>
<td>NR</td>
<td>0.1 mM</td>
<td>10</td>
<td>0.1</td>
<td>10</td>
<td>NR</td>
<td>118</td>
</tr>
<tr>
<td>Desulfovibrio alaskensis (2019)</td>
<td>Ag–Au</td>
<td>20</td>
<td>Spherical</td>
<td>20 µL</td>
<td>20 µL</td>
<td>0.1</td>
<td>6-7</td>
<td>NR</td>
<td>119</td>
</tr>
<tr>
<td>Waste tea leaves extract (2021)</td>
<td>Au–Ag</td>
<td>5–12</td>
<td>Spherical</td>
<td>0.3 mL</td>
<td>30</td>
<td>2</td>
<td>~5</td>
<td>NR</td>
<td>120</td>
</tr>
<tr>
<td>Pulicaria undulata (2020)</td>
<td>Ag–Fe</td>
<td>30</td>
<td>Quasi spherical</td>
<td>5 mg</td>
<td>20</td>
<td>0.2</td>
<td>45</td>
<td>1.1²</td>
<td>121</td>
</tr>
<tr>
<td>Polysaccharide extracted from Ramaria botrytis mushroom (2020)</td>
<td>Ag–Au</td>
<td>150</td>
<td>Spherical</td>
<td>30.27 mg mL⁻¹</td>
<td>30</td>
<td>0.057</td>
<td>14</td>
<td>3.6²</td>
<td>122</td>
</tr>
<tr>
<td>Punica granatum extract (2015)</td>
<td>Au–Ag</td>
<td>12</td>
<td>Core–shell</td>
<td>NR</td>
<td>100</td>
<td>5</td>
<td>6</td>
<td>13.3²</td>
<td>123</td>
</tr>
<tr>
<td>Silybum marianum seed extract (2015)</td>
<td>Au–Ag</td>
<td>20–200</td>
<td>Spherical</td>
<td>0.5 mL</td>
<td>15</td>
<td>2</td>
<td>24</td>
<td>NR</td>
<td>124</td>
</tr>
<tr>
<td>Ginger rhizome powder (2018)</td>
<td>Cu–Ag</td>
<td>1.6–26</td>
<td>Spherical</td>
<td>10 mg</td>
<td>500</td>
<td>1</td>
<td>10</td>
<td>4.05–6.08</td>
<td>125</td>
</tr>
<tr>
<td>NPs supported on degraded Pueraria mirifica starch (DPS) (2013)</td>
<td>Au–Ag</td>
<td>NR</td>
<td>Spherical</td>
<td>0.3 mL</td>
<td>15</td>
<td>0.2</td>
<td>35</td>
<td>NR</td>
<td>116</td>
</tr>
<tr>
<td><strong>Supported NPs</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NPs synthesized with Cetraria islandica (L.) ash and supported on graphene oxides (2020)</td>
<td>Ag–Au</td>
<td>6–30</td>
<td>Spherical</td>
<td>2.7 mL</td>
<td>100</td>
<td>9.6 × 10⁻⁵</td>
<td>2–3</td>
<td>7.5–11.4</td>
<td>126</td>
</tr>
<tr>
<td>NPs supported on polydopamine-functionalized graphene (2016)</td>
<td>Pt–Au</td>
<td>2.7–6</td>
<td>Spherical</td>
<td>3 mg mL⁻¹</td>
<td>100</td>
<td>0.1</td>
<td>16</td>
<td>9.5</td>
<td>127</td>
</tr>
<tr>
<td>NPs decorated on graphene nanosheets (2014)</td>
<td>Au–Pd</td>
<td>2.67–3.15</td>
<td>Spherical</td>
<td>1.25 µg</td>
<td>10</td>
<td>0.1</td>
<td>25</td>
<td>14.5</td>
<td>115</td>
</tr>
</tbody>
</table>

* NR = not reported. * Denoted values were recalculated for uniformity in the corresponding units with respect to other reports.
mL$^{-1}$. Obviously, the catalytic reduction reaction may take more time if the concentration of NaBH$_4$ is lower, but it is essential to evade boron purification.

4.5.2 Effect of reaction temperature on 4-nitrophenol reduction. To determine the ability of green-fabricated metal catalysts for 4-NP reduction, it is necessary to consider environmental conditions and it is essential to perform temperature-dependent studies. Based on the temperature-dependent 4-NP reduction reaction kinetics, we can also estimate thermodynamic parameters such as entropy, enthalpy, and Gibbs free energy. Sanoe Chairam et al.$^{88}$ tested mung bean starch-mediated AuNPs for the reduction of 4-NP at different temperatures and calculated the activation energy ($E_a$), enthalpy and entropy of 47.42 kJ mol L$^{-1}$, 44.78 kJ mol L$^{-1}$, and 261.49 kJ mol L$^{-1}$, respectively.

4.5.3 Experiments mimicking environmental conditions. To test the efficiency of the fabricated catalysts, the reaction needs to be performed in real (river, marine, agriculture, industry, etc.) water samples. As mentioned in the introduction, 4-NP is also used as a pH indicator, and thus the real water samples contain different pH and several contaminants such as metal ions and pesticides. Thus, the changes in the absorption spectrum can confirm the pH of the real water solution. As is well known, the faster catalytic reduction of 4-NP happens in basic pH medium. On the one hand, there is a possibility of undergoing a faster reaction rate in real water samples (most samples above neutral pH). On the other hand, slower reaction kinetics can be observed due to the presence of unwanted systems such as heavy metals and other pollutants.

Moreover, interference studies need to be performed before using NPs in real-world applications. To the best of our knowledge, there are no studies on real water sample testing using green-fabricated metal nanoparticles.

4.6 Catalytic performance estimation parameters
The kinetics of the reaction can be estimated using the pseudo-first-order reaction, as follows:

$$\ln(C/C_0) = -kt$$

The regression factor ($R^2$) and rate of the reaction can be obtained from the slope ($k$, units: s$^{-1}$ or min$^{-1}$).

$$\ln(C/C_0) \text{ vs. } t$$

where, $C_0$ and $C_t$ indicate the initial and concentration of 4-NP at time $t$, respectively, and $k$ is the apparent rate constant.

Thermodynamic parameters

Gibbs free energy ($\Delta G$) = $\Delta H - T\Delta S$ (1)

From the Arrhenius equation

$$\ln(k) = \left( - \frac{E_a}{R} \right) \frac{1}{T} + \ln(A)$$ (2)

and

$$\ln\left( \frac{k}{T} \right) = \left( - \frac{\Delta H}{R} \right) \frac{1}{T} + \ln\left( \frac{K_B}{h} \right) + \frac{\Delta S}{R}$$

(3)

$$\ln\left( \frac{k}{T} \right) \text{ vs. } \frac{1}{T} : \left( - \frac{\Delta H}{R} \right) = \text{slope}$$

$$\ln\left( \frac{K_B}{h} \right) + \frac{\Delta S}{R} = \text{constant} (c)$$

where $A$ = Arrhenius constant, change in enthalpy ($\Delta H$) and entropy, $R = 8.314$ J k$^{-1}$ mol$^{-1}$, $K_B = 1.381 \times 10^{-23}$ J k$^{-1}$, $h = 6.626 \times 10^{-34}$ J k$^{-1}$ mol$^{-1}$, $T$ = absolute temperature in Kelvin, and $k = k_{app}$ = pseudo-first-order rate constant.

Activity parameter

$$k' = km\text{ units: s}^{-1}\text{ mg}^{-1}$$

where $m$ is the catalyst mass and $k$ rate of the reaction.

Reduction/degradation capacity

$$Q_t = (C_0 - C_t) \times M/m$$

where $C_0$ is the initial and $C_t$ is the concentration of 4-NP at time $t$, $m$ is the mass of the catalyst and $M$ is the mass of the organic pollutant.

Turnover number (TON): the TON is calculated using the number of moles of substrate that 1 mol of catalyst can convert into product.

Turnover frequency (TOF): the TOF is calculated simply by TON/reaction time.

Conversion efficiency

Conversion efficiency (%) = $\frac{C_0 - C_t}{C_0} \times 100$ 

where $C_0$ and $C_t$ are the initial absorbance of the 4-nitrophenol solution and with time ($t$), respectively.

5 Possible mechanistic understanding for the conversion of 4-nitrophenol to 4-aminophenol

The catalytic reduction of 4-NP by NaBH$_4$ and metal catalysts was investigated with the possible reaction mechanism presented in Fig. 3 initially following the LH model. The ionization of sodium borohydride in the liquid phase results in the production of borohydride ions (BH$_4^-$) and their adsorption on the surface of the metal catalyst to form a metal hydride.
Simultaneously, 4-nitrophenol adsorbs on the metal hydride complex surface. Given that the progress is reversible, adsorption is followed by the desorption process. Thermodynamic equilibrium on the hydride complex surface allows H2 transfer from the hydride complex surface to 4-NP, followed by the formation of the 4-nitrophenolate ion (4-NP−).

Even though the specific mechanism still needs to be understood, according to the available hypothetical concepts, two (direct and condensation) paths can be proposed for the conversion of 4-nitrophenol to 4-aminophenol in the presence of NaBH4 and catalyst. In the direct path, there is a possibility to obtain two consecutive fast reactions, i.e., nitro group to nitroso group formation, and then amine group. Similarly, the condensation path involves the formation of azoxy compounds through the condensation of hydroxylamine with the nitroso compound. This is followed by its reduction, azoxy to hydrazo and hydrazo to 4-AP.

6 Challenges and future perspectives

In conclusion, green-fabricated metal nanoparticles and their up-to-date advancements in the reduction of 4-nitrophenol exhibited escalated progress in the past two decades. However, some challenges still need to be addressed for their possible scalability and application as economically viable water purifiers. Besides the production approach for developing highly stable and efficient metal nanoparticles, absorption in the entire visible spectrum and narrow bandwidth of metal nanoparticles with monodispersity and uniformity are required for specific applications and enhanced catalytic activity. Incredibly, researchers are still struggling to find possible economically viable techniques/methods for purifying metal nanoparticles and confirming the reduction of 4-nitrophenol.

The use of green materials from recycled waste needs to be assessed to produce metal nanoparticles. In addition, it is necessary to understand the effect of the presence of biomass on the development of metal nanoparticles. Alternatively, rapid and simple procedures are essential to develop recyclable catalytic probes to boost catalytic efficiency. We suppose that the forthcoming investigation of catalytic probes using sustainable precursor-based metal nanoparticles will expand the general audience and scientific community awareness of their pollution removal application because of their simplicity, accessibility, and compatibility.

Conflicts of interest

There are no conflicts to declare.

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