A new study of biomediated Pd/tiO₂: a competitive system for *Escherichia coli* inhibition and radical stabilization

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Abstract

Successive resistance towards most of the antibacterial agents is a serious threat to global health and food security. There is an immense need to synthesize new materials with enhanced anti-pathogenic activity. Here we report a green-oriented fabrication method to produce Pd doped TiO₂ nanocomposite using 15 ml of *Phoenix Sylvestris* extract that plays an important role in the formation and stabilization of Pd/TiO₂. Green synthesized Pd/TiO₂ was characterized using various spectroscopic techniques i.e. FTIR, XRD, HRTEM, SEM, and EDS. The morphological and size measurements were performed by HRTEM and SEM analysis. The data obtained confirmed that phytochemicals in plant extract play a significant role in the formation and stabilization of Pd/TiO₂ nanomaterial. Moreover, the biogenic Pd/TiO₂ was found to be crystalline in nature, and the palladium was well dispersed on the surface of titanium dioxide. Furthermore, Pd/TiO₂ synthesized at 15 ml leaf extract showed strong antibacterial activity (18 mm diameter of zone of inhibition) against *Escherichia coli* (*E. coli*). The results obtained from MIC (i.e. 0.062 mg ml⁻¹), Reactive oxygen species (ROS), no hemolytic risk and antioxidant activity (i.e. 86% trapping of DPPH) further ascertain the efficiency and biocompatibility of the Pd/TiO₂ nanomaterial. The strong antibacterial activity of Pd/TiO₂ is ascribed to the smaller size and spherical morphology of palladium nanoparticles that offers a large surface area and more active sites to interact with the targeted molecules.

1. Introduction

Nanoscience has offered an extraordinary manipulation and understanding of matter at the atomic and molecular level, leading to amplified consistency of knowledge, technology, and education. The objectives of nanotechnology are to enhance understanding of nature, expanded productivity, cultivating living standards of the modern era and to provide better alternatives for various issues of diverse fields of science and industry. Nanoparticles show some amazing properties such as large surface area, high diffusion, and penetration, controllable size and morphology, high magnetic susceptibility and biocompatibility [1–4]. These properties escalate the practicability of nanotechnology among various technologies.

To obtain diversified morphology and size of nanoparticles, various distinctive synthetic techniques have been employed since last few decades. Despite the fact that these strategies come up with convincing outputs yet a key understanding of better manufacturing process is required that could have a practical applicability in the industry at a commercial level. Considering this situation, green approach is an exceptionally suitable alternative. Biodirected synthesis of metals, metal oxides, and metal nanocomposites is safer, economic, non-toxic, and eco-friendly than the other typical physical and chemical methods [5–7]. Some of these physical and
chemical methods include sol-gel method, chemical reduction method, thermal decomposition method, co-precipitation method and hydrothermal method etc [8–16].

A variety of green synthesized metal and metal oxide nanoparticles have been synthesized with diversified applications such as a catalyst in various reactions, in medical diagnostics and treatment of diseases, in wastewater treatment and as antibacterial/antimicrobial agents [17–25] etc.

Formerly, palladium nanoparticles using various plant species such as Talinum triangulare, Mussaenda glabratia, Rosa damascene, Urtica dioica, and Thymus vulgaris, Prunus japonica, and Alysicarpus monilifer have been reported [26–30]. The reported work demonstrates the use of Phoenix Sylvestris (a tree from the family Fabaceae) leaf extract to fabricate palladium decorated titanium dioxide nanomaterial. Phoenix Sylvestris is widely used in herbal treatment of many diseases among various countries of South East Asia. Several research works have highlighted its medicinal importance against different microbial infections [31–35]. Different volumes of plant extract were used to optimize the formation of palladium nanoparticles thus the bio-mediated PdNPs synthesized at optimal conditions have been examined for their antibacterial and antioxidant activity against E. coli and DPPH respectively.

2. Materials and methods

2.1. Characterization

The bio-mediated Pd/TiO₂ was primarily analyzed using the following analytical techniques. A Rigaku D/Max 2500 VBZ+/PC diffractometer was used to determine XRD measurements. An ABB MB3000 spectrophotometer was used to perform the FT-IR analysis. A JEM-3010 microscope was utilized for HRTEM analysis. SEM and EDS analysis were done by a Hitachi S-4700 scanning electron microscope. The microscope (Olympus 1 × 51) was used to obtain fluorescence images at 488 nm and 535 nm i.e. excitation and emission wavelength respectively.

2.2. Preparation of phoenix sylvestris plant leaf extract

Phoenix Sylvestris plant was collected from Lakki Marwat, Pakistan. To prepare the leaf extract firstly, they were unruftled and cleaned by washing them meticulously with distilled water to remove dust and other unwanted materials. The washed leaves were then dried and pulverized into fine powder. About 8 g plant leaves were added to 100 ml of distilled water and the resulting suspension was heated at 70 °C for 5 h over a magnetic shaker. The suspension was then filtered and the filtrate was kept in the freezer to use next.

2.3. Synthesis of TiO₂ nanoparticles using extract of phoenix sylvestris

3 mM solution of TiO(OH)₂ was magnetically stirred in 100 ml distilled water for 1 hr at 80 °C in order to obtained homogenous suspension. 15 ml extract of Phoenix Sylvestris was added to this homogenous suspension of TiO(OH)₂ while stirring at room temperature for 5 h. After that the suspension was filtered and washed with distilled water and dried in vacuum oven at 70 °C for 5 h. The prepared nanomaterial was then calcined at 300 °C for 5 h to obtained TiO₂ nanoparticles.

2.4. Green synthesis of Pd/TiO₂ using extract of phoenix sylvestris

To synthesize Pd/TiO₂ nanomaterial, 2 g of the prepared TiO₂ was first stirred in 100 ml deionized water in order to obtain a true suspension. 2 mM solution of PdCl₂ was prepared and added drop wise to the homogenous suspension of TiO₂ with continues stirring. Subsequently, 15 ml of leaf extract of the said plant was added to the above solution at constant stirring for 6 h at 60 °C temperature. Formation of Pd/TiO₂ nanomaterial was indicated by a change in color from light yellow to dark brown. It was then centrifuged at 6000 rpm to collect the Pd/TiO₂ pellet. Finally, the nanomaterial was kept in an oven for drying at 80 °C for 3 h.

2.5. Agar well diffusion screening

To evaluate the antimicrobial efficiency of the bio-mediated Pd/TiO₂ nanoscale material, they were screened against Escherichia coli by agar well diffusion process. The bacterial strain was cultured on nutrient agar plates and treated with biogenic Pd/TiO₂ at 37 °C for 24 h. Then, 25 µl of Pd/TiO₂ nanomaterial solution (1 mg ml⁻¹) was transferred to the wells present on nutrient agar plates and kept for 1 hr at 25 °C. Then, the plates were incubated for 24 h at 37 °C. The antibacterial activity of Pd/TiO₂ was expressed in terms of zone of inhibition (mm).

2.6. Determination of MIC

The least amount of an antimicrobial material that prevents or resists the growth of the microorganism is regarded as MIC. Serial dilution method was employed to examine the minimum inhibitory concentration of
Pd/TiO₂ fabricated using 15 ml plant extract. 2 mg of bio-fabricated Pd/TiO₂ was added to 2 ml of bacterial solutions (Escherichia coli) in sterilized test tubes with 0.5 Mcfarland turbidity standard. Then the tested sample was incubated for 24 h at 37 °C. The test tube containing bacterial culture was used as a control.

2.7. Generation of reactive oxygen species (ROS) by Pd/TiO₂
DCFH-DA-kit was used to evaluate the production of ROS by green synthesized Pd/TiO₂. DCFH-DA is a reduced fluorescein that is used to spot various ROS within the cell such as OH, O₂, and H₂O₂. In a typical assay, a mixture of bio-mediated Pd/TiO₂ (prepared at optimized condition) and the bacterial strain (i.e. Escherichia coli) was incubated for 2 h at 250 rpm. Subsequently, the bacterial cells suspension was obtained by centrifugation at 4,000 rpm for 10 min. The pellet obtained was then washed twice with phosphate buffer saline. Phosphate buffer containing a suspension of the pellet was treated with 25 mM Dichloro-dihydro-fluorescein diacetate (DCFH-DA) reagent in 1:1 ratio for 30 min. Finally, the excess dye was washed away from the surfaces of the cells using PBS.

2.8. Hemolytic activity of bio-mediated Pd/TiO₂
In order to evaluate the hemolytic property of green synthesized Pd/TiO₂ nanomaterial prepared using 15 ml plant extract, the amount of hemoglobin ejected from RBCs was determined on treatment with Pd/TiO₂. The blood sample from a male albino rat was used for model examination. The blood sample was kept into a sterile Lithium Heparin Vacutainer. Then it was centrifuged at 4000 rpm for 20 min. The pellet was then obtained by removing the supernatant carefully. The pellet thus obtained was sterilized thrice with Phosphate Buffered Saline (PBS). PBS solution was maintained at pH 7.4 and different amounts of green synthesized Pd/TiO₂ (i.e. 20, 50, 80, 110, 140 and 170 μg) were added in (5% v/v) PBS solution with the total volume up to 1 ml. RBCs in PBS solution were used as a negative control while RBCs in 1% Triton X-100 solution were used as a positive control. The reaction mixtures were incubated at 37 °C for 1 h in a shaking incubator. Then the tubes containing the above mixture were centrifuged at 1000 rpm for 20 min and the resulting supernatant was examined at 540 nm against their blank.

3. Result and discussion
3.1. Fourier transform infrared spectroscopic analysis
The effect of capping, reducing and stabilizing functional groups found in the plant source can be clearly indicated by FTIR spectroscopic analysis. Figure 1 represents the FTIR spectrum of green synthesized Pd/TiO₂ nanomaterials. FTIR spectrum indicates three prominent peaks i.e. at the 1020 cm⁻¹, 1600 cm⁻¹, and 3388 cm⁻¹. A broad peak at 3388 cm⁻¹ is a characteristic peak for hydroxyl group (–OH) that confirms the presence of phenolic groups in the organic moiety. The remaining two peaks at 1020 cm⁻¹ and 1600 cm⁻¹ reflect C=C and C=N stretching frequencies, respectively. A declined peak intensities effect in case of Pd/TiO₂ can be attributed to the association of these functional groups during the synthesis of the said nanomaterial. Such results have already been reported [36].

3.2. X-ray diffraction analysis
To confirm crystallinity of Pd, TiO₂ and Pd/TiO₂, XRD analysis was performed. Figure 2 specifies the XRD pattern of biogenic the said nanomaterials. The XRD spectrum was obtained at angle 2θ range set at 20°–80°.
Figure 2(a) indicates four prominent Bragg’s peaks in XRD spectrum obtained at 38°, 44.5°, 64° and 78° correspond to (111), (200), (220) and (311) lattice planes of an f.c.c crystal structure for greener PdNPs. The most important peak obtained at 39° can be credited to f.c.c crystal structure of palladium nanoparticles. XRD spectrum depicts the importance of (111) crystal planes in biogenic PdNPs due to a high atomic concentration that makes (111) crystal plane as a highly reactive facet. A similar result has already been reported in a research work [37]. Figure 2(b) indicates nine well resolved peaks around 25.2°, 37.6°, 48.0°, 54.2°, 55.2°, 62.6°, 69.1°, 70.3° and 77° which correspond to the existence anatase form of TiO2. In case of Pd/TiO2 nanocomposite (figure 2(c)) a small peaks appeared at Pd position along with the titanium oxide peaks which clearly shows that PdNPs are well uploaded on the titanium surface.

3.3. High resolution transmission electron microscopic analysis
HRTEM analysis was performed to determine size, morphology, and dispersion of biogenic Pd/TiO2. Figure 3(a) exhibits the image obtained by HR-TEM analysis. HRTEM analysis confirms that Pd/TiO2 fabricated using 15 ml plant extract exhibit the ideal morphology. The Pd nanoparticles are highly dispersed, almost spherical in shape on the surface of TiO2. The average size of Pd nanoparticles was analyzed to be less than 10 nm. The result illustrates that TiO2 is a good support for Pd nanoparticles. Such results have been reported previously [38].

3.4. Scanning electron microscopic analysis
The size and morphology of biogenic Pd/TiO2 was also examined through SEM. Figure 4(a) represents the SEM image of said Pd/TiO2. SEM image reflects that the PdNPs are spherical in shape with no major aggregation that is attributed to the extra stability offered by the capping agents present in plant extract and highly dispersed over TiO2 surface and TiO2 which in turn helps to enhance the activity of nanomaterial.

3.5. Electron diffraction spectroscopic analysis
Elemental composition analysis of bio-fabricated Pd/TiO2 was performed as expressed in figure 4(b). EDS analysis indicates an intense palladium peak along with a carbon peak that confirms the effective role of capping and stabilizing agents from the organic moieties present in plant extract. The organic moieties present in plant source not only reduce the Palladium ions and help in the formation of PdNPs but also stabilize them by the interaction between the functional groups and nanoparticles. Besides palladium and carbon and oxygen, a major peak for titanium has also detected by EDS detector.
3.6. Applications

3.6.1. Antibacterial activity of Pd/TiO₂

Increased resistance of various pathogens towards most of the available drugs may lead to a serious limitation of the available drugs to be used as therapeutics. New therapeutic materials must be synthesized and applied to hamper the activity of such microbial pathogens. To overcome the increasing resistance of available drugs green synthesized Pd/TiO₂ were evaluated for antibacterial activity against *Escherichia coli*. The diameter of the zone of inhibition for green synthesized Pd/TiO₂ verifies that the antibacterial activity of bio-mediated Pd/TiO₂ highly depends upon the morphology and size of the nanoparticles. The Pd/TiO₂ NMs synthesized at 15 ml plant extract show highest anti-bacterial activity (i.e. 18 mm diameter of zone of inhibition (Table 1) supplementary figure 1 is available online at stacks.iop.org/MRX/6/125430/mmedia) as compared to the individual nanomaterial i.e. PdNPs and TiO₂. *Escherichia coli* is a Gram-negative bacterium. Former studies indicate that PdNPs damage bacterial membrane, penetrate into the bacterial cytoplasm and leads to the production of various reactive oxygen species (ROS), which can damage DNA and other cellular components. Moreover, the phytochemicals found in the organic part of various therapeutic plants exhibit the astonishing characteristic to reduce the metal ions into nanomaterial, which shows encouraging activity against microbes such as bacteria, viruses, fungi, and protozoan. [39–43]. Figure 5(a) indicates the morphology of bacterial cells (*Escherichia coli*) before treatment with biogenic Pd/TiO₂ nanomaterial, figure 5(b) shows bacterial cells (*Escherichia coli*) after the treatment with biogenic Pd/TiO₂ nanomaterial. The results support the antibacterial activity of Pd/TiO₂ nanomaterial by the denaturation and shrinkage of the bacterial cell on treatment with green synthesized

![Figure 3](image1.png) Figure 3. High-resolution transmission electron microscopic (HRTEM) analyses of biogenic (a) Pd/TiO₂ and (b) particle size distribution.

![Figure 4](image2.png) Figure 4. (a) Scanning electron microscopic (SEM) analysis of green synthesized Pd/TiO₂ and (b) EDS analysis.
reactive oxygen species interact with cell bodies and cell membrane leading to cell lysis. The antibacterial activity of Pd/TiO$_2$ nanomaterials were also compared with biosynthesized silver nanoparticles as shown in table 2.

### 3.6.2. Determination of MIC

MIC is related to the quantitative measurement of the efficiency of any material against a micro-organism (e.g. bacteria). It is an effective method to determine the extent of resistance offered by an antimicrobial agent against the visible growth of a microbial agent in artificial media when incubated for a specific time. To further examine the antibacterial activity, the biogenic Pd/TiO$_2$ nanomaterial synthesized at optimized conditions was screened for MIC. The bacterial strain (Escherichia coli) immersed in a dilute suspension of Pd/TiO$_2$ was incubated overnight and the MIC was recorded as 0.62 mg (table 3). The result obtained indicates that such a minute amount of as-synthesized Pd/TiO$_2$ are quite effective as an antibacterial agent.

### 3.6.3. Generation of reactive oxygen species by Pd/TiO$_2$

In order to understand the possible mechanism for the antimicrobial activity, the greener Pd/TiO$_2$ were examined for ROS production within the microbial cell. Figures 6(a), (b) shows the presence of intracellular ROS.
before after the treatment with Pd/TiO$_2$. The intensity of ROS after treatment with greener Pd/TiO$_2$ has increased inferring the high efficiency of green synthesized Pd/TiO$_2$ mainly depends on the ROS production in the cellular space of micro-organism. The reactive functional groups from the phytochemicals from the plant source as well as the highly energetic electrons from the PdNPs contribute to the production of various reactive oxygen species such as OH$^\cdot$, O$_2^\cdot$, and H$_2$O$_2$ in the microbial cell. These reactive species may lead to elevate the oxidative stress in the microbial cell. The increasing oxidative stress induces the destruction of intracellular species at the molecular level. These biomolecules and cellular organelles such as DNA, RNA, mitochondria, cell membrane and various cellular proteins when damaged may lead to the death of the cellular body of microorganism. In the presence of ROS 2, 7-dichlorofluorescein-diacetate oxidizes to dichlorofluorescein and produces fluorescence (green) upon excitation at 488 nm.

### 3.6.4. Hemolytic activity

An antimicrobial agent must exhibit some peculiar properties before its direct application such as its biocompatibility with normal cells, particularly with RBCs. So, RBCs were treated with certain concentrations of Pd/TiO$_2$ at optimal fabrication condition (i.e. 20, 50, 80, 110, 140 and 170 μg). All of the examined concentrations were found to exhibit no hemolytic activity for RBCs and had an approximately same hemolytic activity to negative control as presented in table 4. The biocompatibility of bio-oriented Pd/TiO$_2$ can be associated with the functional groups present in the organic moiety from the plant source that induces the plasma antiradical efficiency. That, in turn, declines the tendency of erythrocytic membranes to undergo oxidation and hence manifests the hemolytic resistance.

### 3.6.5. Antioxidant activity

An oxidant or a radical is a species that urges to actively react with other species, mostly electron rich specie that is able to donate an electron or more to the radical to stabilize it. Such antiradical or antioxidants must exhibit a strong reducing ability. In order to evaluate the reducing and scavenging ability of green synthesized Pd/TiO$_2$, they were made to reduce DPPH radical. DPPH is a stable organic free radical that resists undergoing radical

![Figure 6](image.png)

**Figure 6.** ROS production (a) before treatment with bio-mediated Pd/TiO$_2$ and (b) after treatment with bio-mediated Pd/TiO$_2$.

| Sample (μg) | Hemolytic activity (%) (OD$_{540\text{ nm}}$) |
|------------|------------------------------------------|
| Control    | 1.33 ± 0.1                                |
| 1% Triton X-100 | 98 ± 0.0                                |
| Pd/TiO$_2$ (20 μg) | 1.35 ± 0.11                              |
| Pd/TiO$_2$ (50 μg) | 1.4 ± 0.11                               |
| Pd/TiO$_2$ (80 μg) | 1.41 ± 0.11                              |
| Pd/TiO$_2$ (110 μg) | 1.45 ± 0.12                              |
| Pd/TiO$_2$ (140 μg) | 1.51 ± 0.11                              |
| Pd/TiO$_2$ (170 μg) | 1.59 ± 0.13                              |

OD$_{540\text{ nm}}$ is optical density at 540 nm.

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oriented polymerization. Therefore, DPPH is used as an experimental substrate to check the antioxidant efficacy of bio-fabricated Pd/TiO2 nanomaterial. A range of Pd/TiO2 concentrations i.e. 0.3–1.5 mg l⁻¹ was added to 1 ml of 1 mM DPPH solution in dark under constant stirring. Vitamin C was used as a blank and as a standard respectively. UV spectroscopic measurements were performed to monitor the scavenging and trapping efficiency of Pd/TiO2 after incubation by applying the formula,

\[
\% \text{ inhibition} = \frac{\text{Abs}_{\text{control}} - \text{Abs}_{\text{test}}}{\text{Abs}_{\text{control}}}
\]

Where, \(\text{Abs}_{\text{control}}\) and \(\text{Abs}_{\text{test}}\) are absorbances of control and substrate respectively.

Figure 7(a) represents the antioxidant efficiency of Pd/TiO2. The greener Pd/TiO2 donates electrons to DPPH radicals that is not only indicated by the decrease in absorbance maxima of DPPH at 517 nm but also by the decolorization of the solution. The experimental data obtained explains that the highest antioxidant activity (i.e. 86%) was analyzed in case of Pd/TiO2 nanomaterials as compared to individual PdNPs (79%) and TiO2 (75%). Such a high efficiency of Pd/TiO2 depends upon several factors such as the size, morphology and concentration of PdNPs, synergic effect and also phytochemicals present on their surface. Moreover, the antioxidant activity of nanomaterials increases with the increase in concentration of the nanomaterial. Thus the efficient antioxidant activity of Pd/TiO2 further validates the robust biocompatibility and functionality of Pd/TiO2 in living environment in terms of a trapping the oxidants to improve the body defense system.

4. Conclusion

In the modern era, green nanotechnology is comes out to be the most trending technology to fabricate nanomaterials. The broad band applications of green nanotechnology can be correlated with its several positives such as the use of non-toxic chemical, eco-friendly, safe and non-critical reaction setups. The reported research work illustrates a bio-mediated route to fabricate Pd/TiO2 using Phoenix Sylvestris plant extract. The phytochemicals present in the plant leaf extract play a key role in reducing, capping and stabilizing agents. The as-synthesized Pd/TiO2 nanomaterial, the palladium nanoparticles are of small sized, almost spherical shaped.
and good dispersion with no considerable aggregation. Biogenic Pd/TiO2 exhibited promising antibacterial activity and MIC against Escherichia coli, with no hemolytic activity. Moreover, Pd/TiO2 demonstrated strong antioxidant activity that further verifies the bio-functionality of nanomaterial. Further examination is required to explore some unique properties of bio-mediated Pd/TiO2.

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