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FULL PAPER

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A green synthesis of palladium nanoparticles by *Sapindus mukorossi* seed extract and use in efficient room temperature Suzuki–Miyaura cross-coupling reaction

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A simple and green method for the synthesis of palladium nanoparticles using an aqueous extract of *Sapindus mukorossi* seed has been demonstrated. The synthesized nanoparticles were characterized using UV–visible spectroscopy, powxder X-ray diffraction, energy-dispersive X-ray analysis and transmission electron microscopy. The nanocatalyst was successfully utilized in an efficient Suzuki–Miyaura cross-coupling reaction at room temperature.

KEYWORDS
boronic acid, palladium nanoparticles, *Sapindus mukorossi*, Suzuki–Miyaura

1 | INTRODUCTION

The Suzuki–Miyaura cross-coupling reaction is considered to be one of the most elegant and powerful tools for constructing C─C bonds, particularly in the formation of biaryls – a structural motif found in many products of commercial importance.[1,2] Since the first report of palladium-catalysed Suzuki coupling of aryl halides and arylboronic acids,[3] the reaction has undergone tremendous developments as far as the catalyst, reaction conditions and substrate scope are concerned. Now, it has reached a status of respect in modern chemistry. The credit can be attributed to the mild reaction conditions involved and also due to the tolerance to wide varieties of functional groups. The catalytic system used for such coupling reaction is generally either Pd(0) or Pd(II) species, in some cases together with suitable phosphine- or nitrogen-based ligands.[4] Owing to the sensitivity of the catalytic species to oxygen and moisture, the palladium-catalysed Suzuki reaction is generally performed under inert atmosphere or involving hazardous organic solvents. On the other hand, availability, stability and cost of the palladium species are the main drawbacks of this reaction. However, from the green chemistry perspective, environmentally friendly solvents such as water,[5] ionic liquids[6] or supercritical carbon dioxide[7] are considered to be more favourable alternatives compared to organic solvents.

This is an era of emergence and applications of nanocatalysis due to the peculiar size-dependent properties of nanoparticles (NPs).[8] Often, this high catalytic activity is attributed to high surface area of NPs compared to the bulk counterparts. Pd NPs of various shapes and sizes are generally prepared using a variety of chemical and physical methods. In wet chemical methods, Pd NPs are synthesized via the reduction of Pd(II) species in the presence of stabilizing agents,[9] capping agents or solid supports, which can control both their size and morphology.[10] Though the synthesized Pd NPs show excellent catalytic activity, there are some demerits associated with these methods. Examples are the requirement of high temperature, ultrasonication, etc., thereby making the process tedious and time-consuming, contamination from precursor chemicals, use of toxic solvents and formation of by-products which are environmentally not benign. Common physical methods for their synthesis include attrition and pyrolysis involving large energy input.[11] Consequently, there are continuing demands for the development of green and eco-friendly routes for the synthesis of NPs in a single synthetic step with minimum loss of chemicals in environmentally friendly solvents.

Biological feedstocks such as plant extracts, microorganisms, etc., can be used for the synthesis of NPs[12] as they have the required potential for the reduction of Pd(II) to Pd(0).[13] The advantages of biological methods over

conventional methods are that they are single-step processes, do not require toxic chemicals or high energy and also have diverse biomedical applications such as in nanomedicine. Generally, NPs are thermodynamically unstable leading to agglomeration and a resulting appreciable decrease in the catalytic activity of the NPs. Therefore, to stabilize the NPs various stabilizers such as surfactants, organic ligands (such as sulfur-, phosphine- and nitrogen-based ligands), polymers and dendrimers are used.[14] Additionally, sulfur-based ligands are associated with a poisoning effect.[15] But, in our case, we have not used any kind of stabilizer; the functional groups present in the biomolecules of soapnut shell extract might stabilize the resulting Pd NPs. Hence, nowadays, these cost-efficient and environmentally friendly processes are highly significant and can easily be scaled up.

Working in this direction, we recently synthesized Pd NPs@poly(ethylene glycol) from *Colocasia esculanta* leaf extract which could efficiently catalyse the Suzuki–Miyaura cross-coupling reaction.[16] Continuing our endeavour, here we report the generation of Pd NPs using *Sapindus mukorossi* (*S. mukorossi*) seed extract and their utilization in Suzuki–Miyaura cross-coupling reactions of aryl halides and boronic acids without using any ligand. The *S. mukorossi* plant is easily available in the northeastern region of India. *S. mukorossi* fruit, locally known as 'monisol' or 'ritha' (Figure 1), appears in the months of July–August and ripens by November–December. The ripe seeds can be stored for years after drying. The dried seeds are also available in the market throughout the year. Although the utility of *S. mukorossi* fruit as natural surfactant and medicine dates back to ancient times and still exists in several folklores, few scientific reports have appeared recently, which are not extensive and detailed. The extract from the dried pericarp of the soapnut has been studied and characterized for its saponin content and surfactant property by Balakrishnan *et al.*[17] The literature shows its application in essential oil recovery[18] and also in the synthesis of Ag NPs,[19] Au NPs[20] and nanohydroxyapatites.[21] Based on the available reports, we attempted the synthesis of Pd NPs, believing that the extract from *S. mukorossi* would act as a reducing agent as well as an efficient surfactant to stabilize the Pd NPs.

The aqueous extract of *S. mukorossi* fruit pericarp (soapnut shell) is composed of mainly saponins (natural surfactants), flavonoids and carbohydrates.[22] The native people of Asia mainly used soapnut for washing. In addition, these constituents have some medicinal properties such as anti-inflammatory[23] and antimicrobial activity.[24] These constituents are responsible for its suitable reduction potential. Reddy and co-workers[20] synthesized Au NPs using *S. mukorossi* fruit pericarp (soapnut shell) extract and evaluated their catalytic activity for reduction of *p*-nitroaniline.

2 | EXPERIMENTAL

2.1 | Green synthesis of Pd NPs from *S. mukorossi* seed extract

At first, soapnut shells were collected, cleaned and shade-dried. After complete drying they were ground using a domestic blender. The soapnut shell powder was first characterized using energy-dispersive X-ray (EDX) analysis to determine the elemental composition (Figure 2). The EDX analysis shows the presence of potassium (K) in addition to carbon (C) and oxygen (O). However, the amount of K is very low (0.69%) compared to C and O. Further, flame photometry test confirmed the presence of low amount of K (0.046%).

For the preparation of plant extract, 10 g of the finely ground seeds was stirred in a beaker for about 30 min in 60 ml of distilled water at 60 °C, which was then filtered with a muslin cloth at ambient temperature. The filtrate aqueous extract was kept for further experiments.

For the preparation of Pd NPs, 10 ml of the prepared extract was added to 25 ml of 1 mM $Pd(OAc)_2$ solution. The solution was then refluxed at 100 °C in an oil bath for 2 h. The colour of the solution gradually changed from light brown to dark black indicating the formation of NPs. The prepared NPs were separated by centrifuging at 12 000 rpm for 15 min. The separated Pd NPs were washed with distilled water and ethanol, to ensure the NPs were free from biomaterials, and dried in an oven at 60 °C for 2 h.

FIGURE 1 Images of *Sapindus mukorossi* plant and dried seeds

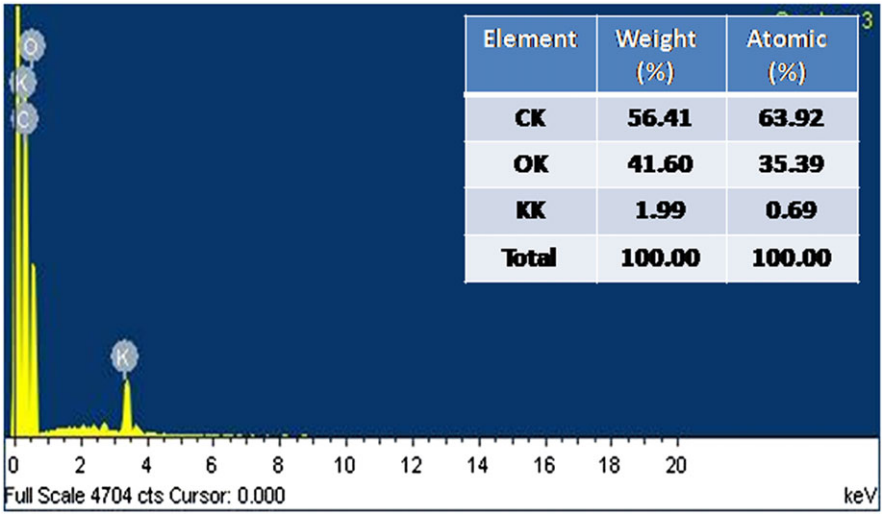
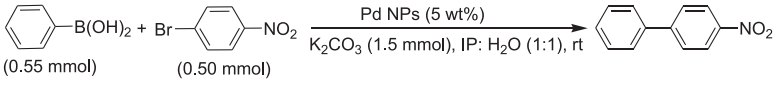


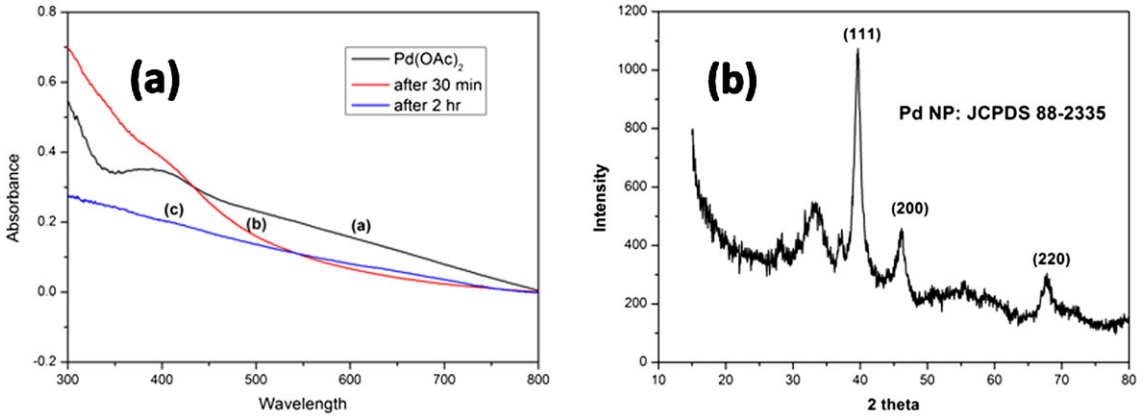
FIGURE 2 EDX analysis of ground *S. mukorossi* seed

2.2 | General procedure for Suzuki–Miyaura coupling reaction

To study the effectiveness of the catalyst in Suzuki–Miyaura reaction, phenylboronic acid and *p*-bromonitrobenzene were chosen as model substrates (Scheme 1). In a 50 ml round-bottomed flask, a mixture of *p*-bromonitrobenzene (0.5 mmol), phenylboronic acid (0.55 mmol), K_2CO_3 (1.5 mmol) and nanocatalyst (5 wt% with respect to boronic acid) was added and stirred in isopropanol–water (1:1) solvent system at room temperature for the required time. The reaction was monitored by TLC. After completion of the reaction, the mixture was diluted with water and the product was extracted with distilled ethyl acetate (three times). The



SCHEME 1 Model reaction for Suzuki–Miyaura cross coupling reaction



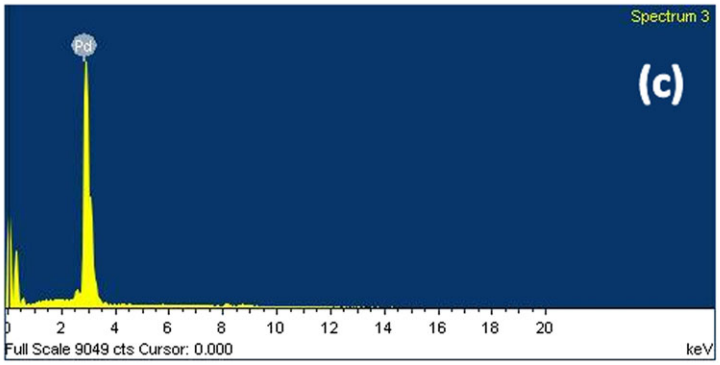


FIGURE 3 (a) UV–visible spectra, (b) XRD pattern and (c) EDX pattern of biosynthesized Pd NPs

combined extract was washed with brine (three times) and dried over Na_2SO_4. The product was purified using column chromatography with silica gel (60–120 mesh) and ethyl acetate–hexane solvent mixture.

3 | RESULTS AND DISCUSSION

3.1 | Characterization of Pd NPs

To confirm the formation of Pd NPs in the presence of the soapnut shell extract, the solution was examined after 30 mins and after 2 h with the help of UV–visible spectroscopy. In the UV–visible spectra (Figure 3a), the peak near 400 nm corresponds to Pd(II) of the aqueous solution of $Pd(OAc)_2$ dissolved with a few drops of ethanol. However, as time progresses, with the formation of Pd NPs, the peak near 400 nm begins to disappear and vanishes completely in 2 h, suggesting the complete reduction of Pd(II) to Pd(0) and indicating the formation of Pd NPs.

The crystalline nature of the synthesized Pd NPs was determined using the powder X-ray diffraction (XRD) technique From the XRD pattern (Figure 3b), three distinct picks are observed at 40.010°, 46.040° and 67.790° which

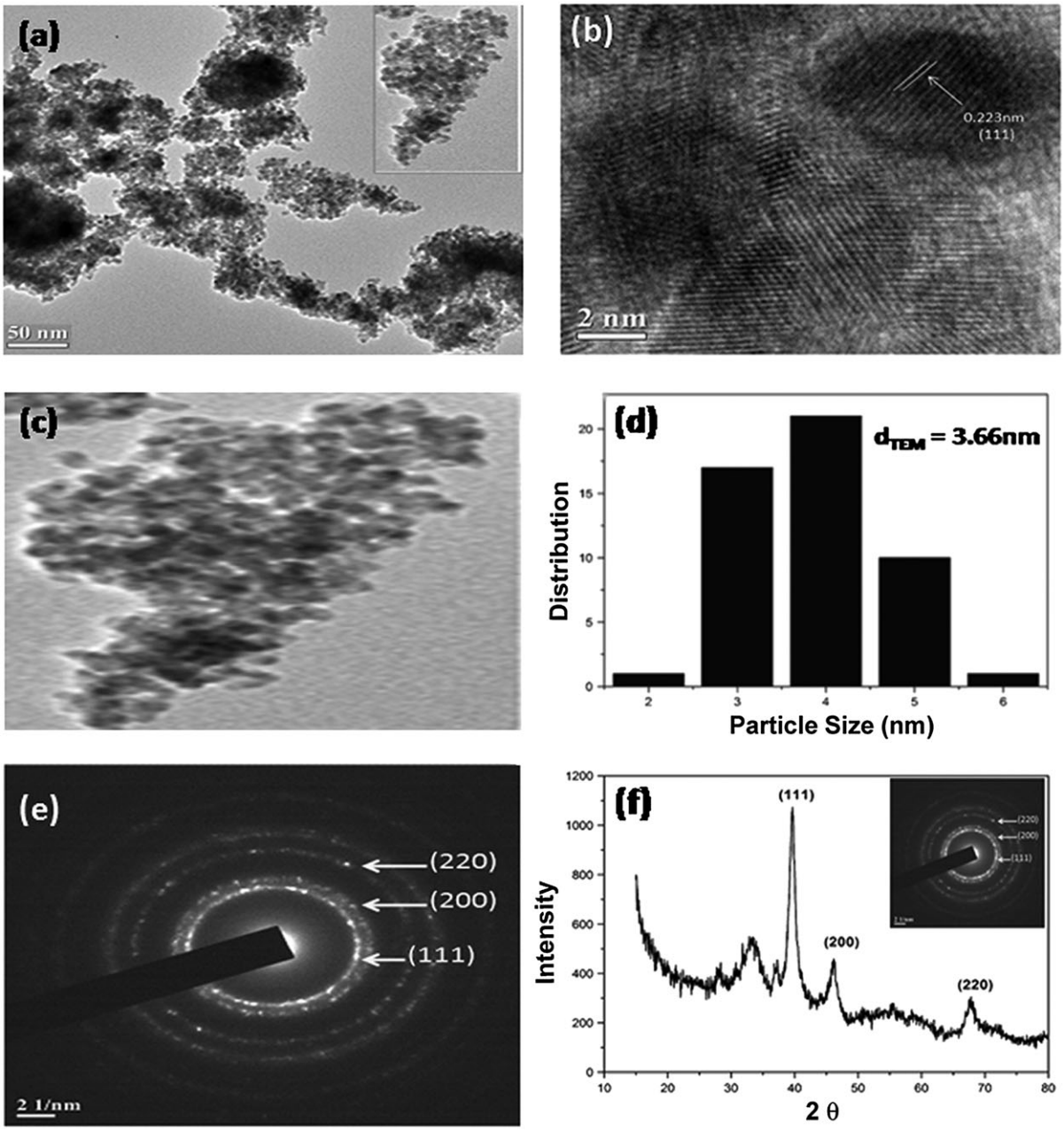


FIGURE 4 (a) TEM and (b) HRTEM images of Pd NPs, and (c) portion from where particle size distribution is calculated. (d) particle size distribution, (e) SAED pattern and (f) comparison of SAED and XRD patterns of Pd NPs

correspond to (111), (200) and (220) planes, respectively, that can be indexed to face-centred cubic phase of Pd NPs (JCPDS no. 88–2335). The broadening of the XRD peaks indicates that the synthesized particles are in the nanometric range. EDX analysis of the Pd NPs reveals the presence of Pd signal devoid of any other metal impurities as shown in Figure 3(c).

The Pd NPs were characterized for size and shape using transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) observations (Figure 4). From the TEM image, we can say that the NPs preferentially crystallize in a spherical shape. The inter-planar distance of 0.223 nm as calculated from the HRTEM image (Figure 4b) corresponds to (111) plane of Pd NPs. The size distribution of the NPs (Figure 4d) shows that most of the particles fall in the size range of 3–5 nm and the mean particle diameter is about 3.6 nm. The smaller the size of the NPs, the greater is their surface area. Because of this high surface area the synthesized Pd NPs show high catalytic performance. The small nanosized particles add to the bare surface area of the active component of the catalyst, thereby increasing the contact between reactant and catalyst and enhancing the catalytic activity. The diffraction dots observed in the selected area electron diffraction (SAED) image (Figure 4e) proves the crystalline nature of the synthesized Pd NPs and the crystal lattices corresponding to the (111), (200) and (220) planes are clearly visible. Figure 4(f) shows a comparison of the XRD planes and the SAED pattern.

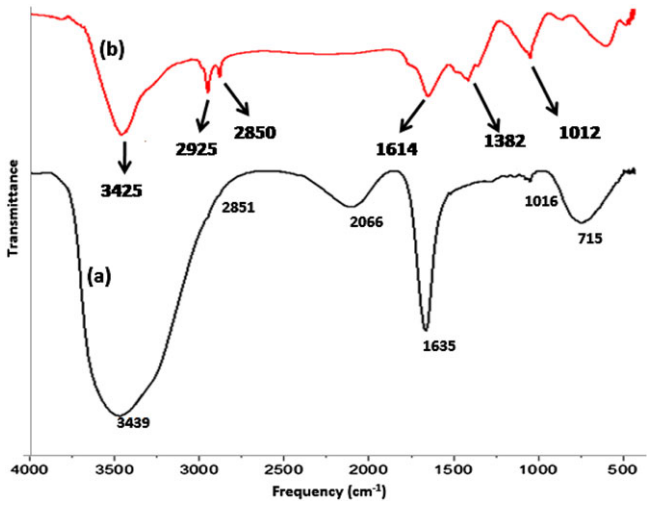


FIGURE 5 Fourier transform IR spectra of (a) soapnut shell extract and (b) Pd NPs

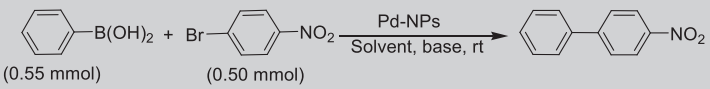
3.2 | Role of soapnut shells in Bioreduction process

The aqueous extract of soapnut shells has high contents of saponins and flavonoids. These biomolecules have numbers of hydroxyl groups that participate in the reduction of Pd(II). The bioreduction of Pd(II) might occur through the oxidation of hydroxyl groups to carbonyl groups:

$$Pd(II) + 2R{-}OH \rightarrow Pd(0) + 2R{=}O + 2H^{+}$$

In the infrared (IR) spectrum of the plant extract (Figure 5a), the peak observed at 3439 cm^{-1} is due to O—H

TABLE 1 Optimization of reaction condition for catalyst, solvent and extract



Entry	Amount of catalyst (wt%)	Solvent	Base (1.5 mmol)	Time (h)	Yield (%)[b]
1	5	No solvent	K_2CO_3	8	15
2	5	H_2O	No base	24	—
3	5	H_2O	K_2CO_3	24	60
4	5	DMF	K_2CO_3	24	74
5	5	MeOH–H_2O	K_2CO_3	24	80
6	**5**	**Isopropanol–H_2O**	**K_2CO_3**	**0.5**	**94**
7	5	Isopropanol–H_2O	Na_2CO_3	1.5	90
8	5	Isopropanol–H_2O	KOH	2.5	85
9	3	Isopropanol–H_2O	K_2CO_3	3	82
10	8	Isopropanol–H_2O	K_2CO_3	0.5	94
11	10	Isopropanol–H_2O	K_2CO_3	0.5	94
12[c]	5	Isopropanol–H_2O	K_2CO_3	0.5	87

[a]Reaction conditions: phenylboronic acid (0.55 mmol), 4-bromonitrobenzene (0.50 mmol), rt.

[b]Isolated yield.

[c]1 mmol of base was used.

stretching vibration of saponins or flavonoids. A low-intensity peak at 2851 cm^{-1} maybe due to carboxylic O—H bond stretching of saponins or flavonoids.[20] The presence of C═C groups in saponins is supported by the appearance of a peak at 1635 cm^{-1}.[25] Further, the appearance of a peak at 1016 cm^{-1} indicates the presence of ester groups in saponins.[25] The peak at 2066 cm^{-1} is due to C—H stretching vibration of sugar present in the soapnut shell extract.[16] The hydroxyl groups present in the aqueous extract of soapnut shells primarily reduces Pd(II) to Pd(0). The appearance of peaks at 2850, 1614 and 1012 cm^{-1} in the IR spectrum of Pd NPs (Figure 5b) indicates that the resulting Pd NPs might be stabilized by the functional groups present in the biomolecules of soapnut shell extract.

After confirmation of the formation of Pd NPs, we attempted to find suitable reaction conditions for the coupling protocol. For that, the reaction of 4-bromonitrobenzene and phenylboronic acid was chosen as the model reaction. It is worth mentioning that the system shows excellent catalytic activity for coupling of inactivated aryl bromides with phenylboronic acids in isopropanol–water (1:1) at room temperature. The results are summarized in Table 1.

An initial screening of the effect of solvents using K_2CO_3 (1.5 mmol) as base showed that isopropanol–water (1:1) was the most effective one, affording excellent yield (Table 1, entry 6). The presence of base is also very essential for the reaction, as the reaction does not proceed in the absence of base (Table 1, entry 2). In the presence of other inorganic bases like Na_2CO_3, KOH, etc., the reaction also proceeds with comparable yield of the cross-coupling product (Table 1, entries 7 and 8). Then, we optimized the reaction condition for the amount of the catalyst and found that 5 wt% of Pd NPs is the optimum amount. For optimizing the amount of base, we tried the same reaction with 1 mmol of K_2CO_3 (Table 1, entry 12) and the yield decreased to 87%. Thus, the best reaction conditions for the formation of biaryl are with 5 wt% of the catalyst in isopropanol–water (1:1) solvent and in the presence of K_2CO_3 (1.5 mmol) base at room temperature (Table 1, entry 6).

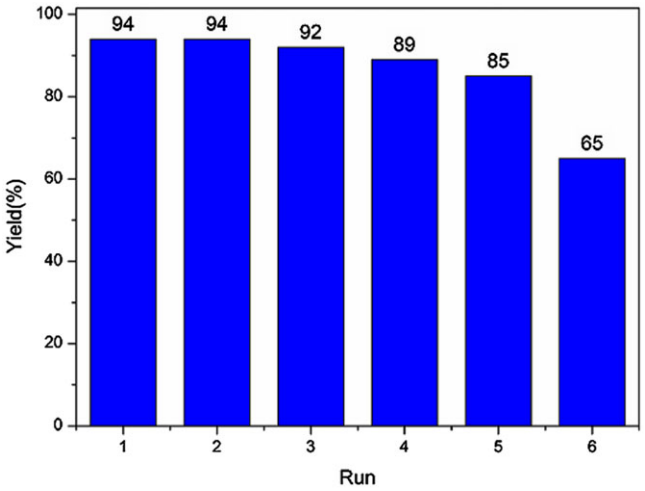
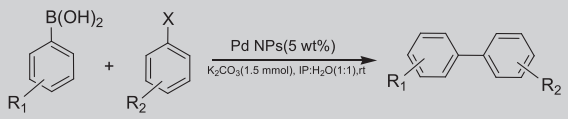


FIGURE 6 Reusability of Pd nanocatalyst.

TABLE 2 Suzuki–Miyaura cross-coupling reactions of various aryl halides and arylboronic acids catalysed by Pd NPs



Entry	R_1	R_2	X	Time (min)	Yield (%)[b]
1	H	H	4-Br	30	95
2	H	H	4-I	20	96
3	H	NO_2	4-Br	30	94
4	H	OCH_3	4-I	15	85
5	4-Cl	NO_2	4-Br	45	95
6	4-OCH_3	H	4-Br	50	81
7	4-OCH_3	OCH_3	4-I	25	98
8	4-Me	OCH_3	4-Br	40	89
9	4-CHO	H	4-Br	40	89
10	4-CHO	OCH_3	4-Br	80	85
11	4-$COCH_3$	H	4-Br	80	85
12	4-$COCH_3$	OCH_3	4-I	65	85
13	4-F	OCH_3	4-Br	80	89

[a]Reaction conditions: aryl bromide or iodide (0.5 mmol), arylboronic acid (0.55 mmol), Pd NPs (5 wt%), K_2CO_3 (1.5 mmol), rt, in air.

[b]Isolated yield.

To evaluate the scope and limitation of the reaction procedure, wide varieties of electronically diverse aryl halides with arylboronic acids were examined using the optimized reaction conditions. The results are summarized in Table 2. It is obvious that cross-coupling reaction between aryl halides and arylboronic acids with different electron-withdrawing and electron-donating groups is effected smoothly by the synthesized Pd NPs. However, with arylboronic acid bearing electron-donating groups (Table 2, entries 6–8), the reaction proceeds smoothly requiring less reaction time as compared to arylboronic acid bearing electron-withdrawing groups (Table 2, entries 10–12).

Again, from the green chemistry point of view, the reusability of the catalyst is an important principle. Accordingly, to examine the reusability of our catalyst in the Suzuki–Miyaura cross-coupling reaction, 4-bromonitrobenzene (1 mmol) and phenylboronic acid (1.1 mmol) were chosen as the model substrates (Scheme 1). After completion of the

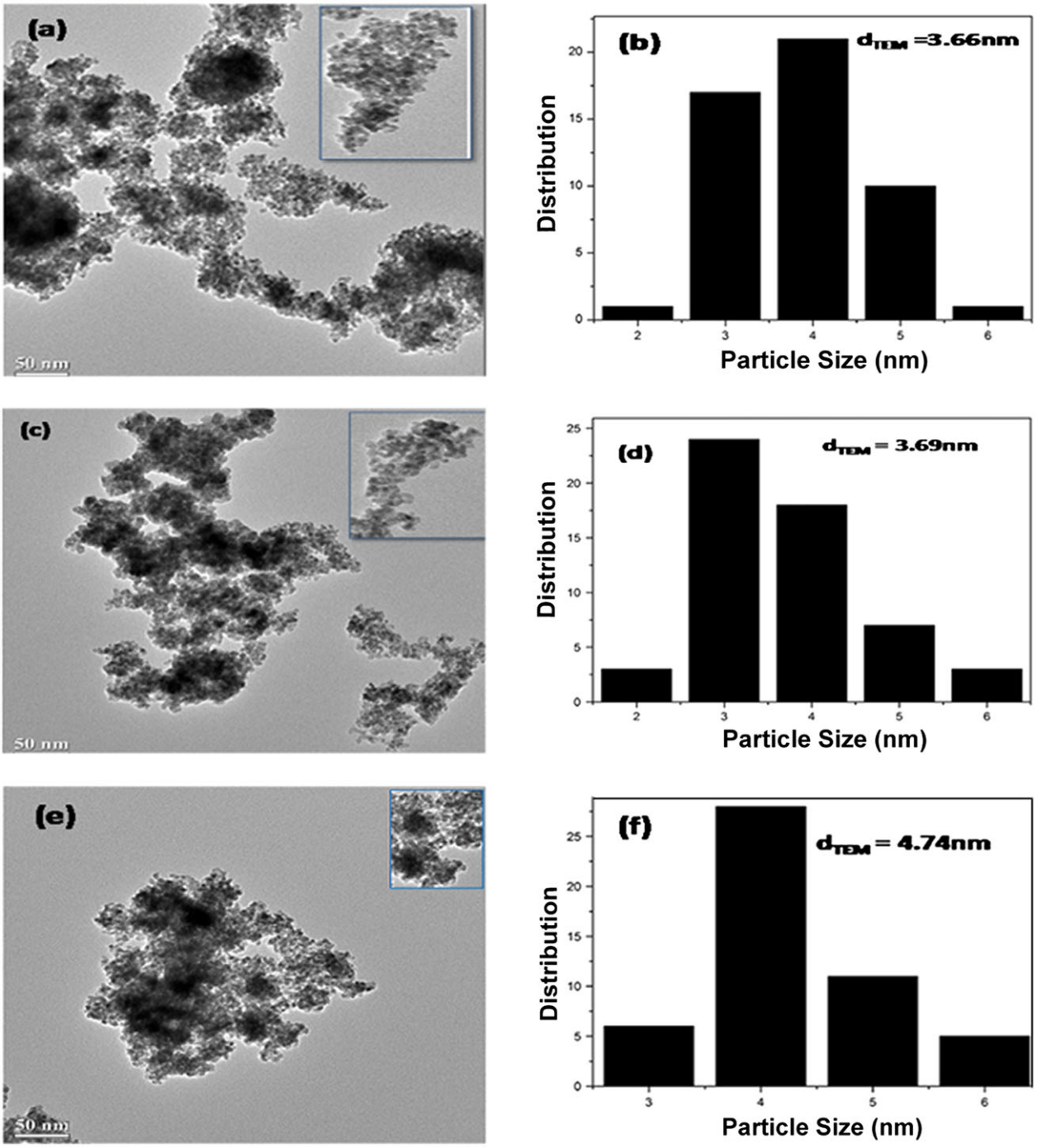


FIGURE 7 TEM images of Pd NPs (a) before the reaction, (c) after second cycle and (e) after fifth cycle. (b, d, f) corresponding particle size distributions

reaction, the reaction mixture was filtered through Whatman 40 filter paper. The catalyst being insoluble remained as a residue in the filter paper. It was then collected and dried in an oven at 60 °C. The collected Pd NPs were placed in a round-bottomed flask and a fresh reaction with the same amount of starting material was carried out. We found that the catalyst was reusable up to the fifth cycle with slight loss of catalytic activity (Figure 6). After the fifth cycle the catalytic activity decreased sharply which might be due to deactivation of the catalyst during the course of reaction and recovery process. Here, to ascertain the stability of the Pd NPs, we employed TEM imaging technique before and after the Suzuki reaction. Figure 7(a) shows a TEM image of the Pd NPs before the reaction. The corresponding particle size distribution is presented in Figure 7(b). (Figure 7a and b are identical to Figure 4a and 4d, respectively.) Figure 7(c) and (d) show TEM image of Pd NPs after the second cycle and the corresponding particle size distribution, respectively. We found that there is no change of particle size of the NPs before and after the second cycle (comparing Figure 7b with d). The TEM image and corresponding particle size distribution of the NPs after the fifth cycle are shown in Figure 7(e) and (f), respectively. The average size of the NPs as calculated from Figure 7(f) is 4.74 nm. In principle, the catalytic activity of the nanocatalyst is determined by the size of the NPs. The smaller the NP size, the greater is the catalytic activity. As the size of the NPs increases after the fifth cycle, the catalyst loses its catalytic activity. It may happen that the stabilizing effect of the biomolecules present in the soapnut shell extract over the surface of the Pd NPs deteriorates after the fifth cycle and therefore aggregation of Pd NPs takes place and consequently the size of the nanoparticles become larger. This results in a decrease of the catalytic activity of the Pd NPs.

3.3 | Hot filtration test

The hot filtration test is a technique generally used to check the heterogeneity of a reaction. For that, the model reaction was again performed under optimized reaction conditions. After 15 min, the reaction was stopped. At this point, the reaction was approximately 51% complete. After removal of the catalyst through filtration, the filtrate was subjected to the same reaction conditions for an additional 10 h. But, no significant increase in the yield of the cross-coupled product was observed (Figure 8). which proves the heterogeneity of the catalyst.

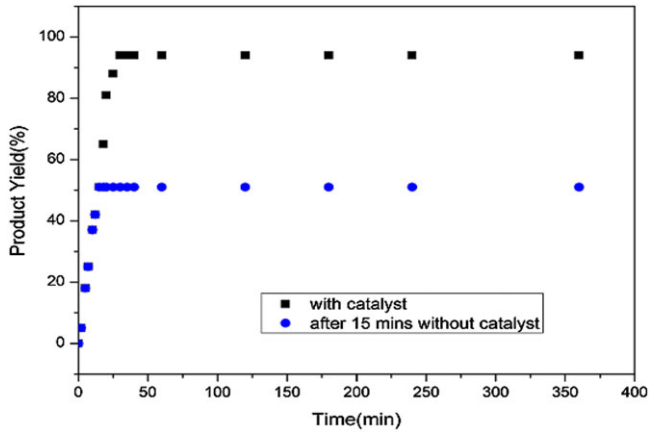


FIGURE 8 Hot filtration test of catalyst.

4 | CONCLUSIONS

We have developed an efficient and green process for the synthesis of Pd NPs using *S. mukorossi* seed extract. The catalyst exhibits excellent catalytic activity under mild conditions for Suzuki–Miyaura cross-coupling reaction at room temperature without addition of any ligand. Furthermore, the reaction takes much shorter time as compared to some of the conventional methods[26] and is also compatible with a wide range of functional groups. The saponin and flavonoid compounds present in the soapnut shell are considered to be responsible for the reduction of Pd(II) which eliminates the need for toxic reducing agents. Therefore, we can consider the process for the synthesis of Pd NPs as a green synthesis. The protocol might be useful for the synthesis of other transition metal NPs.

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