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Magnetic apple seed starch functionalized with 2,2'-furil as a green host for cobalt nanoparticles: Highly active and reusable catalyst for Mizoroki–Heck and the Suzuki– Miyaura reactions

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Funding information Semnan University From the perspective of green chemistry, in catalytic systems, being low cost and eco-friendly, in addition to high chemical and thermal stability, are requirements of support materials. In this regard, we used apple seed starch as an accessible, nontoxic, and cost-effective support material. In order to take advantage of magnetic separation, the magnetite nanoparticles were chosen as an ideal pair for apple seed starch. Furthermore, during the Schiff base reaction, the magnetic apple seed starch was functionalized with 2,2'-furil along with amine functionality to be used as a bio-support for immobilization of cobalt. The introduction of cobalt had a significant effect on the greenness of the catalyst and reducing its price. FT-IR, TGA, XRD, FE-SEM, TEM, VSM, ninhydrin test, element mapping, AAS, and EDX analysis were applied to characterize the newly prepared catalyst. The effectiveness of this novel Schiff base supported catalyst was evaluated in the Mizoroki-Heck and the Suzuki-Miyaura coupling reactions. High reactivity and selectivity were among the most prominent characteristics of the catalyst as compared to previously reported catalysts. The longevity test and hot filtration showed the ability to use the catalyst at least 5 times and negligible cobalt leaching during the reaction, respectively. This work is the first report on the usage of apple seed starch as a supporting catalyst and 2,2'-furil as a ligand in the catalyst modifications and catalytic activity. Accordingly, this can be the beginning of an attractive way in the design and synthesis of heterogeneous catalysts.

KEYWORDS

apple seed starch, biodegradable support, cobalt nanoparticles, cross coupling reaction, green catalyst, magnetic bio-material

considering how to reduce waste and hazardous substances for more than 30 years. For instance, in synthetic

organic chemistry, much attention has been devoted to

developing a greener and more effective routes for the syn-

thesis of biodegradable catalysts. One of the ways to realize

this goal is to use biocompatible and biodegradable

1 | INTRODUCTION

With mounting concerns over the state of our planet, it is becoming critically important that we reduce our environmental footprint. As ever, science is well ahead of the curve in that respect. In fact, scientists have been

Appl Organometal Chem. 2019;e5075. https://doi.org/10.1002/aoc.5075 materials. Biological macromolecular biopolymers are noteworthy candidates to prospect for supported catalysis because of their unbeatable attributes, such as being chemically stable, renewable, and more eco-friendly comparisons with commercial materials.^[1,2] Polysaccharides are the most abundant and common renewable biopolymers, which can be used to reduce global dependence on fossil fuels and replace synthetic polymers.^[3] From another point of view, given the increasing consumption of energy and products in the world, one of the most useful ways is to use waste materials in line with the principles of green chemistry. For instance, applying waste materials in catalytic field can be a constructive step as far as environment and the economy are concerned.^[4] The wastes can either be used directly as a catalyst or be converted into active catalysts by modifying.^[5] Of course, it is to be noted that not all supports are not suitable for use in catalytic applications. Typically, suitable properties of catalyst support materials are: (i) environmental friendliness, (ii) high chemical and thermal durability, (iii) low cost, (iv) inertness against air and moisture, and (v) ease of chemical modification. Apple seed, rich in starch, can be introduced as a very exciting option, as it has all the desired properties of catalyst support, and it is considered to be biodegradable, and on the other hand, most of the time is disposed of as waste, and there have been limited reports in the literature about its use.^[6,7] To the best of our knowledge, there is no published research on the use of apple seed starch as a catalyst support. Among polysaccharides, amylum is the most considerable non-toxic, biodegradable, and biocompatible bio-polymer.^[1] There is a great quantity of reactive free hydroxyl groups in starch; therefore, order to prepare efficient catalysts, apple seed starch can be either directly used for the immobilization of metal ions through chelate mechanism or easily modified by esterification, oxidation, hydrolysis, or etherification. Meanwhile, magnetite nanoparticles with unique properties such as non-toxicity, magnetic recoverability, and high surface area can be a good pair for the apple seed starch to provide greener supported catalysts. In organic chemistry, a large number of reviews have been published covering Heck-Mizoroki and Suzuki-Miyaura C-C cross-coupling reactions as they are the most fundamental reactions in organic synthesis owing to their application in the synthesis of natural products, numerous drugs, biologically active compounds, and many organic building blocks.^[8,9] Principally, palladium catalysts are used to activate aryl halides for the Heck-Mizoroki^[10] and the Suzuki-Miyaura^[11-13] crosscoupling reactions. Although palladium catalysts are uncompetitive in synthetic versatility, they suffer from disadvantages such as high cost, air sensitivity, and

toxicity of complexes, all of which limit their use in the industry. Therefore, recently, many studies have been conducted to replace them with affordable transition metal catalysts, containing nickel,^[14] iron,^[15] copper,^[16] and cobalt.^[17] Cobalt catalysts are a very good choice owing to their higher catalytic activities, nontoxicity, low-cost, chemical and mechanical stability, and availability.^[18] Accordingly, to improve the Heck-Mizoroki and the Suzuki-Miyaura cross-coupling reactions, a number of important studie have utilized new catalytic systems based on cobalt.^[17,19-25] Development of functional groups on supports such as -SO₃H, -COOH, -NH₂, -CONH₂, and -OH for immobilization of metallic nanoparticles is yet another challenge. In this regard, we are pleased to introduce a new ligand called 2,2'-furil, which, to the best of our knowledge, is yet to be considered as a ligand in the catalyst modifications and catalytic activity in the literature. Regarding our efforts to develop and expand environmentally benign and effective heterogeneous catalysts,^[26-29] we wish to reveal the first successful synthesis of magnetic apple seed starch, and its subsequent modification with 2,2'-furil, denoted as MNP@Seed starch@FR. In the last step of the synthesis of the catalyst, cobalt nanoparticles were successfully supported on MNP-apple seed starch functionalized with 2,2'-furil to prepare MNP@Seed starch@FR-Co as a userfriendly, highly stable, and magnetic-separated catalyst. The performance of the resultant biocatalyst was tested through the use of Mizoroki-Heck and the Suzuki-Miyaura coupling reaction, which revealed excellent reaction activity, selectivity, turn over frequency (TOF), and turn over number (TON).

2 | EXPERIMENTAL SECTION

2.1 | General

The chemicals, reagents, and solvents were purchased from Merck and Sigma-Aldrich chemical companies and were employed without further purification. TLC on commercial plates coated with silica gel 60 F254 was applied for checking the progress of the reactions and the purity of the products. The FT-IR spectra were recorded by a Shimadzu 8400 s spectrometer using KBr pressed powder discs. The thermogravimetric analysis (TGA) was performed using a Du Pont 2000 thermal analysis apparatus heated from 25 °C to 1000 °C at ramp 10 °C/min under air atmosphere. X-ray diffraction (XRD) analysis was done on a Siemens D5000 (Siemens AG, Munich, Germany) using Cu-Ka radiation of wavelength 1.54 °A. FE-SEM–EDX analysis was accomplished using TESCAN MIRA II digital scanning microscope. The amount of cobalt in the catalyst was measured with an Agilent model 240 AA Shimadzu (USA) flame atomic adsorption spectrometer. All measurements were done in an air/acetylene flame, and the Co hollow cathode lamps were used as the radiation sources. The magnetic measurement was carried out in a vibrating sample magnetometer (VSM) (4 inches, Daghigh Meghnatis KashanCo., Kashan Iran) at room temperature. TEM images were collected using transmission electron microscope (TEM; Philips EM 208S-100 KV). Detection of the prouducts was performed by a gas chromatograph (GC-17A, Shimadzu, Kyoto, Japan) equipped with a splitless/split injector and a flame ionization detector. Helium (purity 99.999%) was used as the carrier gas at the constant flow rate of 4 mL min⁻¹. The temperatures of injector and detector were set at 275 °C and 320 °C, respectively. The injection port was operated at splitless mode and with sampling time 1 min. For FID, hydrogen gas was generated with a hydrogen generator (OPGU-2200S, Shimadzu, Kyoto, Japan). A 30 m BP-10 SGE fused-silica capillary column (0.32 mm i.d. and 0.25 μ m film thickness) was applied for separation of PAHs. Oven temperature program was: started from 60 °C, held for 3 min, increased to 190 °C at 20 °C min⁻¹, held for 0 min, increased to 240 °C at 10 °C min⁻¹ and then held for 3 min. A 10.0 µL ITO (Fuji, Japan) micro-syringe applied for the collection of sedimented organic solvent and injection into the GC. The NMR spectra obtained using a Brucker Avance 400 MHz instruments (1H-NMR 400 MHz and 13C-NMR 125 MHz) in pure dimethyl sulfoxide.

2.2 | Catalyst preparation

2.2.1 | Synthesis of Fe₃O₄ nanoparticles

The magnetic (Fe₃O₄) nanoparticle was synthesized based on a reported method.^[30] 3 mL of FeCl₃.6H₂O (2 M dissolved in 2 M HCl) was mixed with 10.33 mL of ultrapure water. In the next step, 2 mL of Na₂SO₃ (1 M) was dropwise added into the prior solution in 1 min under magnetic stirring. After mixing the solutions, a complex of SO₃²⁻and Fe³⁺ was formed, changing the color of the mixture from light yellow to red. After the color of the solution returned, it was added to 80 mL NH₃·H₂O solution (0.85 M) under intense stirring. A black precipitate was quickly formed, which was allowed to completely crystallize for another 30 min under magnetic stirring. The magnetic nanoparticles were then purified by a magnetic decantation and washed several times with deionized water (to pH < 7.5). The precipitates were dried in a vacuum oven at 60 °C for 12 h.

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2.2.2 | Preparation of apple seed starch.

Apples were procured from the local supermarket. They were each cut into four pieces and then the fresh seed were separated from other tissues with a knife. The extracted apple seed must be crushed into powder form before use. So, the fresh apple seed were peeled off and disintegrated with a mortar and pestle, and then, to remove the lipid and water, the resulting material washed three times with ethyl acetate and two times with acetone. A vacuum desiccator was used to dry the powder and then stored at 4 $^{\circ}$ C.

2.2.3 | Preparation of magnetic apple seed starch (MNP@Seed starch)

0.5 g of Fe_3O_4 was dispersed in 20 ml of distilled water for 20 min. The prepared apple seed starch (0.5 g) was completely dissolved in 5 ml of distilled water at 80 °C and then added to the uniform mixture of Fe_3O_4 . Then, about 2 to 3 ml of 0.1 M solution of NaOH was added drop wisely to the mixture. The reaction mixture was stirred at 60 °C for 2 hours. At the end, the product was separated by an external magnet, washed with deionized water and ethanol with, and dried at 50 °C.

2.2.4 | Silylation procedure of magnetic apple seed starch (MNP@Seed starch-NH₂)

The amination of the surface of the magnetic apple seed starch was carried out using the method reported in the literature.^[31–37] A mixture of 2 g of MNP@Seed starch and 5 ml of APTES was stirred in 50 ml of dry toluene for 48 hours at 100 °C under a nitrogen atmosphere. After the mentioned time, the NH₂ functionalized magnetic apple seed starch was collected by a magnet, washed with ethanol and dried in an oven at 60 °.

2.2.5 | Schiff base reaction of MNP@seed starch-NH₂ (MNP@Seed starch@FR)

MNP@Seed starch-NH₂ (5 g), 2,2'-furil (5 mmol), and absolute ethanol (100 mL) were transferred to a roundbottomed flask. The reaction mixture was stirred at 60 °C for 24 hours to complete the modification of MNP@Seed starch-NH₂. The imine bond formation was followed by FT-IR. After the Schiff base reaction, the product was separated, washed completely with ethanol, and dried overnight at 95 °C.

2.2.6 | Synthesis of support catalyst for Co nanoparticles (MNP@Seed starch@FR-Co)

In order to immobilize cobalt nanoparticles on MNP@Seed starch@FR, 4.2 mmol of $Co(OAc)_2.4H_2O$ was dissolved in 10 ml of ethanol, and added to a uniform mixture of MNP@Seed starch@FR (1 g) in ethanol (5 mL). The reaction mixture was stirred at 60 °C for 18 hours. The final complex was isolated by a magnet, washed with ethanol several times, and dried at room temperature.

2.3 | Studies on the catalytic activity.

2.3.1 | General procedure for Mizorokiheck reaction catalyzed by MNP@Seed starch@FR-Co

A round-bottomed flask equipped with a magnetic stirrer was charged with 1 mmol of aryl halide, 1.5 mmol of olefin, 4.0 mmol of K_3PO_4 , 0.33 mol% of MNP@Seed starch@FR-Co, and a mixture of DMF (1.5 mL) and H_2O (1.5 mL). The reaction continued for an appropriate time under stirring at 100 °C. After completion of the reaction as followed by TLC, the catalyst was magnetically collected and the reaction mixture was cooled to ambient temperature. The product was extracted by ethyl acetate and dried with MgSO₄. Some products were characterized by comparing their ¹H-NMR and ¹³C-NMR spectra with those found in the literature and the results are represented in supporting information.

2.3.2 | General procedure for Suzuki-Miyaura reaction catalyzed by MNP@Seed starch@FR-Co

A mixture of phenyl boronic acid (1.2 mmol), aryl halide (1 mmol), K_2CO_3 (3 mmol) and MNP@Seed starch@FR-Co (0.11 mol%) was placed in a round bottom flask with 5 ml water:ethanol (1: 1) and stirred at 80 °C for a suitable time. TLC allowed following of the reaction progress. After completion of the reaction, the catalyst was removed from the reaction medium using a magnet. After cooling the reaction mixture to ambient temperature, the product was extracted with ethyl acetate. Then, the organic layer was washed with water and dried by anhydrous MgSO₄. Characterization of some products was done by comparing their ¹H-NMR and ¹³C-NMR spectra with those found in the literature and the results are represented in supporting information.

3 | RESULTS AND DISCUSSION

3.1 | Fabrication and characterization of MNP@Seed starch@FR-co

As already noted above, apple seed starch has not been discussed in catalytic applications despite having unique features. So as to eliminate the void in literature, we synthesized cobalt supported on magnetic-apple seed starch functionalized with a new ligand. The process of biocatalyst production is summarized in Scheme 1, comprising the following steps: a) preparation of apple seed starch, b) synthesis of magnetit nanoparticles, c) formation of magnetic-apple seed starch as a result of prepared apple seed starch reacting with the synthesized nano-Fe₃O₄,d) preparation of NH₂-functionalized magnetic-apple seed starch produced by the reaction between (3-aminopropyl)triethoxysilane and MNP@Seed starch, e) functionalization of MNP@Seed starch-NH₂ with 2,2'-furil, and f) immobilization of cobalt nanoparticles on the surface of the prepared bio-support to prepare a novel green biocatalyst.

AAS analysis determined that the synthesized catalyst contains approximately 1.1 mmol g^{-1} Co. FT-IR, XRD, TGA, FE-SEM, VSM, TEM, ninhydrin test, AAS, element mapping and EDX analysis were used to confirm the structure of the catalyst and its stability before and after the catalytic reaction.

3.1.1 | FT-IR spectra

To investigate the physical structure of the prepared samples, The FT-IR spectra of n-Fe₃O₄, apple seed starch, MNP@Seed starch, MNP@Seed starch-NH2, MNP@Seed starch@FR, and MNP@Seed starch@FR-Co were recorded (Figure 1a-f). The presence of the characteristic absorption bands at about 557 and 570 cm⁻¹ observed in magnetic samples are related to the Fe-O vibrations (Figure 1a, and c-f). The FT-IR spectrum of apple seed starch shows characteristic peaks at 3336, 2952, 1647, 1400, and 700–1400 cm⁻¹ which correspond to stretching vibration of -OH, stretching vibration of -CH, bending vibration of O-H, bending vibration of CH₂, and stretching vibration of C-O, respectively (Figure 1b). In Figure 1c, the integration of the characteristic peaks of the magnetic nanoparticles with apple seed starch represents the successful synthesis of the magnetic apple seed starch. In the spectrum of MNP@Seed starch-NH₂, the bands are observed at 3332 cm⁻¹ (-OH and -NH₂ stretching), 2929 and 2850 cm^{-1} (-CH₂ stretching), 1654 cm⁻¹ (N-H bending), and 1000–1026 cm⁻¹ (Si-OR and O-Si-O stretching) (Figure 1d). The successful



SCHEME 1 Preparation of the catalyst

attachment of APTES on the magnetic apple seed starch was proven due to these important changes. ^[38] In the spectrum of the MNP@Seed starch@FR, the expected vibration band of the imine group is observed at 1647 cm⁻¹. Moreover, the appeared peaks at 1473 and 1558 cm⁻¹ can be ascribed to the stretching vibration of -C=C- of the aromatic ring. Therefore, according to these observations, the Schiff base reaction of the MNP@Seed starch-NH₂ with 2,2'-furil is confirmed. In the spectrum of the MNP@Seed starch@FR-Co, the azomethine band (1647 cm⁻¹) shifts to a lower wavelength (1635 cm⁻¹) and decreases its peak intensity, which is due to the to the strong interaction of functional groups with the Co nanoparticles.^[39] The overall results

indicate that the synthesis of MNP@Seed starch@FR-Co was successfully achieved.

3.1.2 | X-ray diffraction spectra

X-ray diffraction (XRD) analysis was used to obtain evidence for the presence of iron and cobalt. Characteristic peaks at around 30.5°, 35.9°, 43.5°, 53.9°, 57.2°, and 63° 20 are clearly visible in all spectrums, which are related to the inverse cubic spinel structure of Fe_3O_4 .^[28] As it is clear from Figure 2b and c, chemical modification decreased the intensity of the Fe₃O₄ peaks but did not change the phase of magnetit nanoparticles. In Figure 2



FIGURE 1 FT-IR spectra of (a) zn-Fe₃O₄, (b) apple seed starch, (c) MNP@Seed starch, (d) MNP@Seed starch-NH₂, (e) MNP@Seed starch@FR, and (f) MNP@Seed starch@FR-Co



FIGURE 2 XRD pattern of (a) n-Fe₃O₄, (b) MNP@Seed starch@FR, and (c) MNP@Seed starch@FR-Co

b and c, a broad reflection in the region between $2\theta = 15^{\circ}$ and $2\theta = 24^{\circ}$ is related to the seed starch.^[40-42] The XRD pattern of the MNP@Seed starch@FR-Co also shows characteristic diffraction peaks at around $2\theta = 29.9^{\circ}$, 39.5° , 55.4° , and 63.5° which correspond to the cubic phase of cobalt nanoparticles that reveal the crystalline nature of the cobalt species.^[17]

3.1.3 | Thermogravimetric analysis

The representative TGA curves of apple seed starch, MNP@Seed starch, MNP@Seed starch@FR, and MNP@Seed starch@FR-Co are shown in Figure 3. They show two key stages decomposition. The first weight loss zone (under 200 °C) is allocated to the release of molecular water (Figure 3a, b, c). The second weight loss region is obtained at 225–570 °C, which corresponds to the



FIGURE 3 TGA curve of (a) apple seed starch, (b) MNP@Seed starch, (c) MNP@Seed starch@FR, and (d) MNP@Seed starch@FR-Co

decomposition of apple seed starch (Figure 3a, b, c, d). According to Figure 3b, the amount of grafted apple seed starch to the magnetic nanoparticle can be estimated. It appears that the incorporation of apple seed starch in MNP@Seed starch is about 22%. But, in Figure 3c, the amount of loss weight at second region increased after modification of magnetic apple seed starch with APTES and FR (46%). It demonstrates that the synthesis of MNP@Seed starch@FR was carried out successfully. A closer inspection of the TGA curve of MNP@Seed starch@FR-Co shows slightly lower thermal stability after the immobilization of cobalt, which can be due to the interaction of the cobalt species with the ligands^[43] and the catalytic effect of them in the decomposition of the organic moieties.^[37] Also, compared to the remaining mass percentage of MNP@Seed starch@FR (~54%) (Figure 3c), MNP@Seed starch@FR-Co has higher undecomposed content (~62%) (Figure 3d). This amount of difference (~8%) can be attributed to the amount of loaded Co which is relatively consistent with the result of AAS analysis. The eminent thermal stability of the prepared substrate was proved by considering the high temperature required to remove organic layers from the MNP surface.

3.1.4 | Field emission scanning electron microscopy

Scanning electron microscopy was used to highlight and get an insight of the structural changes caused by the chemical modifications and the morphology of the apple seed starch, MNP@Seed starch, and MNP@Seed starch@FR-Co (Figure 4). As evident from the Figure 4, structural changes clearly occurred after coating,



FIGURE 4 FE-SEM images of (a, b) apple seed starch, (c, d) MNP@Seed starch, (e) MNP@Seed starch@FR-Co, and (f) the particle size distribution histogram of MNP@Seed starch@FR-Co

functionalization, and immobilization. What is most apparent is the change in the size of the nanoparticles following each step. These changes indicate that the catalyst development process has been successfully completed. Spherical shape and homogenous distribution are common in all the images. However, in the SEM image of MNP@Seed starch@FR-Co, there is some aggregation of the particles that results from the functionalization and immobilization processes. The particle size distribution from the FE-SEM image indicates that the maximum particle size distributions were in the range of 15–25 nm.

3.1.5 | Energy dispersive X-ray (EDX) analysis

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The formation of the green cobalt catalyst was further corroborated through energy dispersive X-ray studies (Figure 5). In Figure 5, the peaks of iron (related to



FIGURE 5 EDX spectra of MNP@Seed starch@FR-Co

Fe₃O₄), carbon (related to apple seed starch, APTES, and FR), silicon (related to APTES), oxygen (related to Fe₃O₄, APTES, apple seed starch, and FR), and nitrogen (related to APTES) are observed. According to the EDX spectrum of the synthesized catalyst, the presence of the cobalt is also apparent in addition to other elements in the body of the catalyst. The amount of Co-entrapped with the bio-support detected by EDX is 7%.

3.1.6 | Energy dispersive X-ray spectroscopy (EDS) mapping

EDS element mapping was used to evaluate the spatial distributions and density of the support material and cobalt supported onto the MNP@Seed starch@FR (Figure 6). As shown in Figure 6, Co species distributes homogeneously as well as C, N, O, Si, and Fe in the bio-catalyst. These observations indicate that aggregation did not occur during coating, functionalization, and immobilization processes.

3.1.7 | Transmission electron microscopy

Further characterization of the morphology and structure of the catalyst was performed by transmission electron microscopy (TEM) (Figure 7). It was easily observed in Figure 7a, b, c, that the Fe_3O_4 NPs core is well encapsu-



FIGURE 6 EDS element mapping of (a) Fe, (b) Si, (C) C, (d) N, (e) O, and (f) Co



FIGURE 7 TEM images of (a, b, c) MNP@Seed starch, and (d, e, f) MNP@Seed starch@FR-Co

lated by apple seed starch. The TEM images of MNP@Seed starch@FR-Co showed well-defined spherical Co particles and good distribution of them in the catalyst, which, have a good agreement with FE-SEM and EDS results (Figure 7d, e, f). Very similar morphology observation has been previously reported.^[17] All these observations indicate that the magnetic apple seed starch functionalized with 2,2'-furil is a good host and ligand for cobalt nanoparticles.

3.1.8 | Vibrating sample magnetometer

The magnetic properties of bare $n-Fe_3O_4$ and the MNP@Seed starch@FR-Co were measured at room temperature through a vibrating sample magnetometer (VSM) (Figure 8a, b). It can be seen that the Fe₃O₄ nanoparticles are superparamagnetic with magnetic saturation (MS) value of about 70. The magnetic saturation value dramatically decreased to 21 emu/g for MNP@Seed starch@FR-Co nanocomposites. However,



FIGURE 8 Room temperature magnetization curves of (a) n-Fe₃O₄, (b) MNP@Seed starch@FR-Co

the level of catalyst magnetizations is still adequate to strongly respond to an external magnet thorough catalyst recovering.

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3.1.9 | Atomic absorption spectroscopy (AAS) analysis

Finally, atomic absorption spectroscopy was performed to determine the exact loading of cobalt in the catalyst. According to the AAS results, a loading at 1.1 mmol.g^{-1} of Co was calculated in the catalyst, which is in good agreement with the EDX result.

3.1.10 | Ninhydrin test

Ninhydrin can be used for the determination of the presence of APTES on the surface of magnetic apple seed starch, because it can react with a terminal primary amine and produces a purple-blue complex (Ruhemann's purple).^[44] Before doing the test, according to the published procedure,^[45] it was ensured that the un-reacted APTES from the surface of MNP@Seed starch-NH₂ was removed by washing with ethanol. Then, 0.032 g of the sample was sonicated in 5 mL of ethanolic ninhydrin solution (0.175 M) for 30 min and continuously refluxed at 90 °C for 25 min. After the mentioned time, the solution was cooled to room temperature, centrifuged for 10 min at 6000 rpm, and its optical density determined at 580 nm with a UV/Vis colorimetric. Therefore, it was concluded that 3-aminopropyl groups are covalently linked with hydroxyl groups in the surface of magnetic apple seed starch.^[31,46]

3.2 | Application of MNP@Seed starch@FR-Co in C-C coupling reactions

In order to prove the effectiveness of our green catalyst, we were interested to study the catalyst's performance in C—C bond formation *via* Suzuki–Miyaura cross-coupling reaction (Scheme 2) and Mizoroki–Heck cross-coupling reaction (Scheme 3).



SCHEME 2 MNP@Seed starch@FR-Co-catalysed Suzuki-Miyaura reaction



SCHEME 3 MNP@Seed starch@FR-Co-catalysed Mizoroki-Heck reaction

3.2.1 | Optimization of the reaction parameters for the Suzuki–Miyaura coupling reaction

Before investigation of the catalytic activity of the catalyst, optimizing the parameters that have critical effects on the result of the reaction, such as temperature, solvent, base system and amount of the catalyst, are required. So, the Suzuki–Miyaura cross-coupling of iodobenzene (1.0 mmol) with phenyl boronic acid (1.2 mmol) was considered as a model reaction to optimize reaction conditions.

Effect of the amount of the catalyst

The effect of the catalyst on the reaction was investigated by testing different amounts of catalyst in the reaction. As shown in Table 1, the product yield increased gradually with increasing catalyst amount because of the availability of more catalytic sites (Table 1, entries 1–4). As

TABLE 1 Optimization of the reaction parameters for the Suzuki-Miyaura reaction

	Ĉ	+	B(OH) ₂ Catalyst, Base			
Entry	Amount of catalyst (% mol)	Base	Solvent, Temperature Solvent	Temperature (°C)	Time (h (min))	Yield (%)
1	0.05	K ₂ CO ₃	H ₂ O	100	(55)	75
2	0.08	K ₂ CO ₃	H ₂ O	100	(50)	80
3	0.11	K_2CO_3	H ₂ O	100	(45)	90
4	0.22	K ₂ CO ₃	H ₂ O	100	(45)	92
5	-	K_2CO_3	H ₂ O	100	24	-
6	0.001(g) ^a	K ₂ CO ₃	H ₂ O	100	24	15
7	0.001(g) ^b	K ₂ CO ₃	H ₂ O	100	24	Trace
8	0.11 ^c	K_2CO_3	H ₂ O	100	24	35
9	0.11	Na ₂ CO ₃	H ₂ O	100	(50)	90
10	0.11	КОН	H ₂ O	100	(45)	55
11	0.11	NaOH	H ₂ O	100	(45)	50
12	0.11	K_3PO_4	H ₂ O	100	(45)	85
13	0.11	Et ₃ N	H ₂ O	100	(50)	90
14	0.11	K_2CO_3	EtOH	100	(45)	85
15	0.11	K ₂ CO ₃	H ₂ O:EtOH (1/1)	100	(45)	98
16	0.11	K ₂ CO ₃	CH ₃ COOEt	100	(45)	70
17	0.11	K ₂ CO ₃	DMF	100	(45)	75
18	0.11	K ₂ CO ₃	H ₂ O:EtOH (1/1)	80	(45)	95
19	0.11	K ₂ CO ₃	H ₂ O:EtOH (1/1)	60	(50)	85
20	0.11	K ₂ CO ₃	H ₂ O:EtOH (1/1)	R.T	6	-

^aReaction was carried out the presence of Fe₃O₄NPs.

^bReaction was carried out in the presence of MNP@Seed starch@FR.

^cReaction was carried out in the presence of Co(OAc)₂.4H₂O.

shown in Table 1, 0.11 mol% is sufficient to obtain a satisfactory efficiency. In the following, in order to prove the vital role of the catalyst in the Suzuki–Miyaura coupling reaction, the reaction was also performed in the absence of the catalyst, in the presence of Fe₃O₄ NPs, MNP@Seed starch@FR, and Co(OAc)₂.4H₂O, which, as can be seen, did not produce good results (Table 1, entries 5–8).

Effect of base

Since the basic role of base in Suzuki reaction cannot be denied, it should be sought to find the best option as a base for use in the reaction. For this regard, the model reaction was carried out in the presence of several bases and, according to the results, K_2CO_3 was the best choice (Table 1, entries 3, 9–13).

Effect of solvent

Solvents can control chemical reactions thermodynamically and kinetically. Therefore, the choice of a suitable high-performance solvent is important. For this purpose, the reaction progress was tested in the presence of different solvents (Table 1, entries 3, 14–17). The results showed that the reaction was carried out with higher efficiency and shorter time in the presence of a mixture of EtOH and H_2O in 1:1 ratio.

Effect of temperature

Temperature is another parameter that influences the reaction, so it was decided to set the reaction at different

temperatures (Table 1, entries 15, 18–20). With respect to the reaction yields and times, 80 °C was chosen as the optimum temperature.

3.2.2 | Catalytic performance of the MNP@Seed starch@FR-Co on several substrates for the Suzuki-Miyaura reaction

In order to investigate the generality of this new green catalyst and extend the scope of its application in the Suzuki–Miyaura reaction, several aryl halides (aryl iodides, aryl bromides, and aryl chlorides) reacted with phenyl boronic acid (Scheme 2). The findings are shown in Table 2. The order of the leaving group ability of halogens is as follows: I > Br > Cl, thus, the results obtained from Table 2 are logical, and the coupling reactions with aryl iodides are faster than aryl bromide and aryl chloride, and aryl chloride needs more time and the reaction efficiency is lower. The structure of some products was checked using their high-field ¹H-NMR and ¹³C-NMR spectra. Furthermore, turnover numbers (TON) and turnover frequency (TOF) are listed for all products in Table 2.

3.2.3 | Optimization of the reaction conditions for the Mizoroki-heck reaction

Having obtained satisfactory results from the use of this new catalyst in Suzuki-Miyaura reaction, we were

TABLE 2 Suzuki–Miyaura coupling reactions of aryl halides with PhB(OH)2^a

Entry	Aryl halide	Product	Time (min) ^b	Yield (%) ^c	TON	TOF
1			45	95	863	1150
2	H3CO-	H ₃ CO-	45	88	800	1066
3	Br		60	91	827	827
4	H ₃ CBr	H ₃ C-	70	86	781	673
5	O ₂ N-Br	0 ₂ N-	45	93	845	1126
6	IBr	Br	50	92	836	1007
7	────────────────────────────────────		3 h	60	545	181

^aReaction condition: aryl halide (1.0 mmol), phenyl boronic acid (1.2 mmol), K₂CO₃ (3 mmol), catalyst (0.11% mol), and EtOH:H₂O (1:1) (5 mL), at 80 °C. ^bDetected by TLC.

^cIsolated yield.

TON: (turnover number, yield of product/per mol of Co).

TOF: (turn over frequency, TON/time of reaction (hour)).

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stimulated to examine the effectiveness of the synthesized catalyst in the Mizoroki–Heck reaction. First of all, because of the need of performing the reaction in the best of conditions, the reaction between iodobenzene and methyl acrylate was considered as a model reaction to optimize the parameters (temperature, amount of catalyst, solvent, and base).

Effect of amount of catalyst

In order to find the optimal amount of catalyst, the carrying out of the model reaction was investigated in the presence of different amounts of the synthesized catalyst (Table 3, entries 1–4). On the other hand, to prove the activity and specific role of the catalyst, the reaction was performed in the absence of the catalyst, in the presence of Fe_3O_4 NPs, MNP@Seed starch@FR, and

 $Co(OAc)_2.4H_2O$, which did not yield satisfactory results (Table 3, entries 5–8). The best result was obtained in the presence of 0.33 mol% of the catalyst.

Effect of base

Regarding the vital role of base in preventing the formation of homo-coupling product and neutralizing hydrogen halides,^[28] carrying out the reaction in the presence of a suitable base is important. In this regard, after performing the reaction in the presence of different bases, K_3PO_4 was selected as the most suitable base (Table 3, entries 3, 9–13).

Effect of solvent

After analyzing the effect of different solvents on the result of the reaction, the best conditions were found with

+ COOMe Catalyst, Base Solvent, Temperature							
Entry	Amount of catalyst (% mol)	Base	Solvent	Temperature (°C)	Time (h (min))	Yield (%)	
1	0.11	K ₂ CO ₃	H ₂ O	100	(75)	55	
2	0.22	K ₂ CO ₃	H ₂ O	100	(70)	70	
3	0.33	K ₂ CO ₃	H_2O	100	(65)	75	
4	0.44	K ₂ CO ₃	H ₂ O	100	(60)	75	
5	-	K ₂ CO ₃	H ₂ O	100	24	-	
6	0.003(g) ^a	K ₂ CO ₃	H ₂ O	100	24	10	
7	0.003(g) ^b	K ₂ CO ₃	H ₂ O	100	24	Trace	
8	0.33 ^c	K ₂ CO ₃	H ₂ O	100	24	30	
9	0.33	Na ₂ CO ₃	H ₂ O	100	(65)	70	
10	0.33	КОН	H ₂ O	100	(65)	70	
11	0.33	NaOH	H ₂ O	100	(65)	65	
12	0.33	K_3PO_4	H ₂ O	100	(60)	80	
13	0.33	Et ₃ N	H ₂ O	100	(65)	70	
14	0.33	K_3PO_4	EtOH	100	(65)	70	
15	0.33	K_3PO_4	DMF	100	(60)	87	
16	0.33	K_3PO_4	DMSO	100	(80)	60	
17	0.33	K_3PO_4	PEG	100	(80)	55	
18	0.33	K ₃ PO ₄	H ₂ O:DMF (1/1)	100	(55)	92	
19	0.33	K_3PO_4	H ₂ O:DMF (1/1)	120	(55)	94	
20	0.33	K ₃ PO ₄	H ₂ O:DMF (1/1)	80	(65)	80	
21	0.33	K_3PO_4	H ₂ O:DMF (1/1)	R.T	6	-	

TABLE 3 Optimization of the reaction conditions for the Mizoroki–Heck reaction

^aReaction was performed in the presence of Fe₃O₄ NPs.

^bReaction was performed in the presence of MNP@Seed starch@FR.

^cReaction was performed in the presence of Co(OAc)₂.4H₂O.

a mixture of DMF and H_2O in 1:1 ratio as solvent (Table 3, entries 12, 14–18).

Effect of temperature

In order to complete the optimization process, the reaction was followed at various temperatures, which showed an optimal temperature of 100 °C (Table 3, entries 18–21).

3.2.4 | Catalytic performance of the MNP@Seed starch@FR-Co on several substrates for the Mizoroki-Heck reaction

The generality and scope of this new bio-catalyst in the Mizoroki–Heck reaction was studied using a variety of aryl halides with various olefins under the optimized reaction conditions (Scheme 3). The results are depicted in Table 4. Considering the first step of the Mizoroki–Heck reaction (oxidative addition), it will be concluded that the coupling reaction with aryl iodide is faster than aryl bromide and aryl chloride. If we look at Table 4, the results are evidence of this fact. Although aryl chloride reacted for a long time and with low efficiency, but, it should be taken into account that many reported cobalt catalytic systems showed no activity with aryl chloride substrates in the Mizoroki–Heck reaction.^[25,47,48] The high performance of this bio-catalyst can be attributed

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to synergistic good effects of cobalt nanoparticles with ligand which grafted on MNP and good dispersion of cobalt nanoparticles. The identification of the structure of some compounds was carried out using their ¹H-NMR and ¹³C-NMR spectra and according to the results it was found that all products were produced in the form of E-isomers. The calculated TON and TOF values for all products are given in Table 4.

3.3 | Comparison of MNP@Seed starch@FR-Co results with those obtained by other workers for the Mizoroki-Heck

In order to further examine the efficiency of the present catalytic method in the coupling reaction of methyl acrylate with iodobenzene, we compared the performance of the MNP@Seed starch@FR-Co with some of the published heterogeneous (Co, Fe, and Ni) catalysts (Table 5). Some clear advantages of the present catalytic system over other supported catalyst systems are: lower temperature, shorter reaction time, greener media, high product yield, use of safe metal, minimization of metal contamination, easy magnetic separation capability, high recyclability, no need to use additional equipment like microwave oven, using low weight percentage of the catalyst, and low cost.

TABLE 4 Mizoroki–Heck coupling reactions of aryl halides with olefins^a

Entry	Aryl halide	Olefin	Product	Time (min) ^b	Yield (%) ^c	TON	TOF
1		COOMe	COOMe	55	92	278	305
2	Br	COOMe	COOMe	90	85	257	171
3	IBr	COOMe	Br	55	85	257	282
4	H ₃ C-Br	COOMe	H ₃ C COOMe	100	87	263	164
5	CI	COOMe	COOMe	4 h	30	90	22
6		СООВи	СООВи	55	90	272	298
7	Br	СООВи	СООВи	85	85	242	172

^aReaction condition: aryl halide (1.0 mmol), olefin (1.5 mmol), K₃PO₄ (4.0 mmol), catalyst (0.33% mol), DMF:H₂O (1:1) (3 mL), at 100 °C.

^bDetected by TLC.

^cIsolated yield.

TON: (turnover number, yield of product/per mol of Pd).

TOF: (turn over frequency, TON/time of reaction (hour)).

 TABLE 5
 Comparison of results for MNP@Seed starch@FR-Co with those for other catalysts in the coupling of iodobenzene with methyl acrylate

Entry	Catalyst	Solvent	Temperature (°C)	Time (h)	Yield (%)	Ref.
1	Co-NHC@MWCNTs ^a	PEG	80	5	85	[49]
2	SiO ₂ -Fe (acac)	PEG	130	1.5	85	[15]
3	Co-MS@MNPs/CS ^b	PEG	80	1	88	[17]
4	Co@MNPs/CS	PEG	80	1	53	[17]
5	Nano Co	NMP	140	16	85	[23]
6	Co hollow nanospheres	NMP	130	16	73	[22]
7	Co/Al ₂ O ₃	NMP	150	24	56	[24]
8	Co-B	water/DMF (5/5)	130	12	98	[47]
9	Co-IL@MWCNTs ^c	Toluene	100	3	87	[25]
10	Ni (II)-DABCO@SiO ₂	DMF	100	3	97	[50]
11	Nano Co	NMP	120	8	90	[51]
12	MNP@Seed starch@FR-Co	water/DMF (1:1)	100	0.91	92	This work

^aMulti walled carbon nanotubes supported N-heterocyclic carbene-cobalt (II).

^bCobalt immobilized on MNPs-chitosan functionalized with methyl salicylate (Co-MS@MNPs/CS).

^cCobalt nanoparticles supported on ionic liquid-functionalized multiwall carbon nanotubes.

3.4 | Reusability of MNP@Seed starch@FR-Co

From an economic, industrial, and environmental point of view, catalyst recyclability is among the most important features. Therefore, catalyst recycling was tested through conducting the Suzuki–Miyaura reaction of iodobenzene with phenyl boronic acid at the optimized reaction conditions. At the end of each cycle, the catalyst was magnetically separated, washed thoroughly with ethanol and distilled water, and dried in an oven at 60 °C. As shown in Figure 9, the catalyst was able to be reused up to 5 times without a significant reduction in efficiency. No changes were observed in the nature and morphology, and negligible Co-leaching and consistent composition of the catalyst, after 5 time reuse, were fixed using FE-SEM and EDX (Figure 10) analysis, respectively.

3.5 | Leaching

In supported metal catalysts, a major problem preventing the separation and reuse of the catalyst is the leaching of metal ions. In order to prove the heterogeneity of the catalyst, the reaction between iodobenzene and phenyl boronic acid was accomplished under optimal conditions. At half the reaction time, the catalyst was



FIGURE 9 Recyclability in the Suzuki–Miyaura reaction of iodobenzene with phenyl boronic acid under the optimized reaction conditions

separated from the reaction medium using a magnet, after which, the reaction proceeded under the same optimal conditions without adding any fresh catalyst for 2 hours. The reaction progress was controlled by TLC. As expected, no further coupling reaction occurred, indicating that there was no leaching phenomenon here. The heterogeneous nature of the catalyst has been proven by the result,^[17,28] and it can be concluded that the attachment of cobalt to the MNP@Seed starch@FR surface is strong.



FIGURE 10 (a) FE-SEM images, and (b) EDX spectra of the recovered MNP@Seed starch@FR-Co nanocomposite

4 | CONCLUSIONS

The present work is the first to report the use of apple seed starch as a supporting catalyst and its attachment to magnetic nanoparticles. As far as the authors are concerned, the present work is also the first to apply 2,2'-furil as a ligand in the catalyst modifications and catalytic activity. The magnetic apple seed starch-Schiff base support acted as a suitable host for cobalt nanoparticles to synthesize MNP@Seed starch@FR-Co as a novel, highly efficient, inexpensive, low-toxicity, user-friendly, highly stable, and magnetic-separated catalyst. The catalytic performance of the resultant biocatalyst was investigated in Mizoroki-Heck and Suzuki-Miyaura reactions. This novel green catalyst showed high selectivity and reactivity in the reactions and minimized the time and the energy required for the Suzuki and Heck reactions in comparison with other previoualy reported cobalt-catalyzed cross-coupling reactions. Subsequently, desirable reusability for at least 5 times was achieved with negligible cobalt leaching during the reaction. It is noteworthy that, demonstration of the combination of cobalt and organic ligands is very rare, so this phosphine and palladium-free catalyst can be introduced as a high effective and recyclable catalyst which can be used in reactions which require a metal catalysis, such as hydroacylation, functionalization of C - H bonds, Fischer-Tropsch synthesis, and Diels-Alder reaction. The extent of the use of this new biocatalyst will be taken into consideration in our laboratory.

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