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Easy conversion of nitrogen-rich silk cocoon biomass to magnetic nitrogen-doped carbon nanomaterial for supporting of Palladium and its application

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Funding information Research Council of the Semnan University In this study, magnetic nitrogen-doped carbon (MNC) was fabricated through facile carbonization and activation of natural silk cocoons containing nitrogen and then combined with Fe_3O_4 nanoparticles to create a good support material for palladium. Palladium immobilization on the support resulted in the formation of magnetic nitrogen-doped carbon-Pd (MNC-Pd). The prepared heterogeneous catalyst was well characterized using FT-IR, TGA, EDX, FE-SEM, XRD, VSM, and ICP-OES techniques. Thereafter, the synthesis of biaryl compounds was conducted to investigate the catalyst performance via the reaction of aryl halides and phenylboronic acid. Further, the catalyst could be used and recycled for six consecutive runs without any significant loss in its activity.

K E Y W O R D S

magnetic nanoparticles, nitrogen-doped carbon, palladium nanoparticle, silk cocoon, Suzuki-Miyaura cross-coupling reaction

1 | INTRODUCTION

Nowadays, there is a growing tendency to utilize the heteroatom-doped carbon-based materials as a catalyst support,^[1-3] because of easy synthesis procedure, low costs, high surface/volume ratio, perfect chemical and thermal resistance, perfect control over morphological structures, and suitability for noble metals immobilization.^[4] In addition to catalytic applications, they can be used in different areas including sensors, fuel cells and lithium ion batteries electrodes, adsorbents, and supercapacitors.^[5-7] In catalytic applications, heteroatom-doped carbon-based materials have opened a new window for developing new catalysts which can be used in organic synthesis. The nitrogen-containing natural compounds have attracted researcher's attention in order to prepare a nitrogen-doped carbon catalyst.^[8] Recently, the nitrogen-doped carbon with enriched heterogeneous sites and improved porosity has drawn considerable attention as a support for noble metals for

catalytic purposes.^[9,10] The chemical environment of the nitrogen atom is a crucial factor to determine important properties, and it is categorized into two major groups: structural nitrogen (i.e., pyridinic, pyrollic, or quarternary-graphitic nitrogen), chemical nitrogen (i.e., nitrosyl or amine group).^[11] Considering the principles of green and sustainable chemistry, utilizing abundant, inexpensive, and renewable resources to prepare nitrogen-doped carbon compounds would be a desirable goal.^[12] The pyrolysis of nitrogen-rich biopolymers is one of the most suitable procedures for the preparation of the aforementioned substances.^[13,14] Silk, a natural compound made by Bombyx mori, is an environmentally friendly protein-based polymer, and it has been used in textiles industries for thousands of years.^[15] Silk is mainly composed of hydrophobic fibroin as the core. Also, it contains hydrophilic sericin surrounding the fibrous fibroin to cement them together.^[16] As silk fiber is a natural filamentous protein-based polymer, it is made from repetitive amino acid sequences.^[17] Due to high biocompatibility and biodegradability, most researches on silk are concentrated at biomedical and clinical fields.^[18] A silkworm cocoon, complex polymeric fibrous network, is employed as a precursor for carbonization to prepare nitrogen-doped carbon compounds.^[19] In fact, it contains fibroin and sericin providing carbon and nitrogen resources for preparing nitrogen-doped carbon compounds. At the temperature of 350°C, the protein secondary structure comprising *β*-sheet fibroin and α -helix sericin can be converted into sp²-hybridized structure or a hexagonal lattice structure of carbon atoms.^[20] This can improve the thermal stability of the nitrogendoped carbon framework.^[21] Herein, we report a novel and inexpensive procedure to prepare nitrogen-rich carbon materials via a thermal carbonization route under a controlled temperature using B. mori silk cocoons as a carbon and nitrogen resources and potassium hydroxide (KOH) as an activating agent. After KOH pellets are dissolved, the silk surface is saturated with KOH, and the reaction of K⁺ ions with C and O of silk during the high thermal process produces K₂CO₃ pyrolyzed into K₂O and CO_2 . The escaping CO_2 gas bubbles causes the formation of porous structures. Carbonizing silkworm cocoons under a controlled temperature offers several advantages. First, the carbon that comes from silk cocoons is considered a sustainable resource. Second, carbonizing silkderived materials creates a multilayer architecture with hierarchical porous structure saturated with uniformly doped nitrogen. Third, with this synthesis route, there is no need for templates, and activating reagents can be easily removed. So far, silk-derived carbon materials have been used in areas such as supercapacitor and lithium batteries.^[22,23] Nevertheless, its application in catalytic systems, especially organic chemistry, is rarely investigated.^[24,25] This is owing to the fact that there is difficulty in the separation of these nitrogen-doped carbon materials from the reaction medium. So the need to design new modified nitrogen-doped carbon materials is unavoidable in order to overcome the aforementioned drawback. Magnetite Fe₃O₄ nanoparticles have drawn remarkable consideration as a powerful catalyst support due to their unique characteristics including chemical and thermal resistance, low toxicity, simple and inexpensive preparation, large surface area, and simple isolation from the reaction medium by an outer magnet. Importantly, magnetic separation is considered a green procedure making it possible to save energy, time, solvents, and so forth. In fact, the problems of high-speed centrifugation, filtration, or other tedious workup processes have been solved.^[26] By combining nitrogen-doped carbon compounds with magnetic Fe₃O₄ nanoparticles, we can gain the benefits of both systems. According to our knowledge, no report has been published about magnetic catalysts derived from carbonized raw silk which includes both fibroin and sericin.

The Suzuki–Miyaura cross-coupling reaction of aryl boronic acid with aryl halides has received considerable attention as a very useful, preeminent, and powerful method for selective formation of C–C bond in organic synthesis, especially for the preparation of biaryls.^[27–29] A significant number of reviews have focused on these reactions, due to their high impact and experimental importance in the generation of fine chemicals and pharmaceuticals.^[30–32] In this regard, many effective catalytic systems have been designed and developed for this reaction.^[33–37] However, considering both environmental and economic issues, the design and development of phosphine-free palladium catalysts continue to be a serious challenge in organic synthesis and industry.^[38]

This paper is a continuation of previous researches on the synthesis and application of new green separable heterogeneous catalysts.^[39-44] This report shows our efforts to make a novel palladium catalyst using both nitrogendoped carbon materials prepared by hydrothermal carbonization process and as-prepared magnetic Fe_3O_4 as a support. This combination offers benefits of simple separation, great reusability, and perfect ability to load a considerable amount of palladium. Afterwards, the catalyst performance was assessed in the synthesizing of biaryl compounds via reaction of aryl halides and phenylboronic acid.

2 | EXPERIMENTAL

2.1 | Materials and instruments

All chemicals employed in this study were of analytical grade and were bought from Sigma-Aldrich and Merck companies. Silk cocoons were purchased from an online shop "Albatross.ir." The products purity was assessed utilizing TLC with commercial aluminum backed plates of Merck silica gel 60 F254. Fourier transform infrared (FT-IR) spectra were recorded using Shimadzu 8400s spectrophotometer in KBr pellets within a range of 400–4,000 cm⁻¹. X-ray diffraction (XRD) patterns were recorded by Philips using Cu/Ka radiation. Field emission scanning electron microscopy (FE-SEM) images were obtained by TESCAN MIRA II equipped with an energy dispersive X-ray (EDX) spectroscopy. Transmission electron microscopy (TEM) image was obtained with a CM120 microscope (Philips). Magnetic properties were assessed by vibrating sample magnetometry (VSM; Lakeshore 7,407) at room temperature from -10,000 to +10,000 Oe. Thermogravimetric analysis (TGA) was conducted using a DuPont 2000 thermal analyzer operated

over the range of 25° C to 800° C using a heating rate of 10° C/min under air flow. The quantity of palladium placed on the catalyst surface was measured by an inductively coupled plasma optical emission spectrometry (ICP-OES) on a Varian VISTA-PRO.

2.2 | Preparation of NC

First, silk cocoons were boiled in water for 30 min, and then they were washed with water and dried at 60°C for 12 h. In the second step, the silk was exposed to thermal processing in an alumina crucible at 500°C with a heating rate of 5°C min⁻¹ for 30 min. The first thermal process resulted in a solid product that was combined with KOH as an activating reagent by grinding at a ratio of 1:1 (*w*/w). Ultimately, for final carbonization, the mixture was heated in an alumina crucible at 800°C with the previous heating rate under N₂ atmosphere for 2 h. The carbonized product was treated with an aqueous solution of HCl 5% for 12 h, followed by washing with distilled water and drying at 80°C.^[45]

2.3 | Synthesis of MNC

For the synthesis of MNC, 1 g of NC was added to 250 ml of an aqueous solution containing $FeCl_2.4H_2O$ (0.858 g) and $FeCl_3.6H_2O$ (2.33 g). Then, under stirring

and reflux conditions, NH_4OH solution was added to the above mixture, and the reaction proceeded under N_2 atmosphere for 2 h. The reaction resulted in the formation of black precipitates which could be isolated by an external magnet followed by washing and vacuum drying.

2.4 | Synthesis of MNC-Pd

MNC (0.1 g), Pd $(OAc)_2$ (0.005 g), and 50 ml of deionized water were mixed together in a round-bottom flask, and then the mixture was sonicated and stirred for 12 h at room temperature. Next, 5 ml of aqueous NaBH₄ (0.1%w/ w) was added to this solution dropwise to reduce the Pd² + to Pd⁰. The final palladium complex MNC-Pd was magnetically separated and washed by deionized water and ethanol and dried in a vacuum oven at 80°C.

2.5 | Typical procedure for Suzuki-Miyaura reaction using MNC-Pd

A mixture of aryl halide (1.0 mmol), phenylboronic acid (1.2 mmol), K_2CO_3 (3 mmol), and MNC-Pd (0.032 mol%) in 5 ml ethanol:water (1:1) was heated up and stirred at 80°C for different time length (see Table 2). The progress of reaction was monitored by TLC. After finishing the reaction and cooling to room

TABLE 1 Optimization of reaction condition for Suzuki–Miyaura coupling reactions^a

| Entry | Amount of catalyst (mol %) | Base | Temperature (°C) | Solvent | Time (min) | Yield (%) ^b |
|-------|----------------------------|---------------------------------|------------------|-----------------------------|------------|------------------------|
| 1 | - | K ₂ CO ₃ | 80 | H ₂ O | 120 | - |
| 2 | 0.020 | K ₂ CO ₃ | 80 | H ₂ O | 40 | 60 |
| 3 | 0.032 | K_2CO_3 | 80 | H ₂ O | 30 | 70 |
| 4 | 0.064 | K_2CO_3 | 80 | H ₂ O | 30 | 72 |
| 5 | 0.032 | K_2CO_3 | 80 | DMF | 30 | 70 |
| 6 | 0.032 | K_2CO_3 | 80 | CH ₃ COOEt | 30 | 60 |
| 7 | 0.032 | K_2CO_3 | 80 | EtOH | 30 | 80 |
| 8 | 0.032 | K ₂ CO ₃ | 80 | EtOH:H ₂ O (1:1) | 30 | 97 |
| 9 | 0.032 | K_2CO_3 | 60 | EtOH:H ₂ O (1:1) | 30 | 70 |
| 10 | 0.032 | K_2CO_3 | 100 | EtOH:H ₂ O (1:1) | 30 | 97 |
| 11 | 0.032 | K_2CO_3 | r.t | EtOH:H ₂ O (1:1) | 120 | - |
| 12 | 0.032 | Na ₂ CO ₃ | 80 | EtOH:H ₂ O (1:1) | 30 | 85 |
| 13 | 0.032 | КОН | 80 | EtOH:H ₂ O (1:1) | 30 | 50 |
| 14 | 0.032 | NaOH | 80 | EtOH:H ₂ O (1:1) | 30 | 54 |
| 15 | 0.032 | Et ₃ N | 80 | EtOH:H ₂ O (1:1) | 30 | 80 |

Bold values indicate the optimal conditions.

^aReaction conditions: aryl halide (1.0 mmol), phenylboronic acid (1.2 mmol), base (3 mmol), and MNC-Pd.

^bIsolated yield.

| Entry | Aryl halide | Time (min) | Product | Yield ^b (%) | TON | TOF |
|-------|--------------------|---------------|--------------------|------------------------|-------|-------|
| 1 | | 30 | | 97 | 3,031 | 6,062 |
| 2 | H ₃ C- | 35 | H ₃ C- | 90 | 2,812 | 4,848 |
| 3 | H ₃ CO- | 35 | H ₃ CO- | 94 | 2,937 | 5,064 |
| 4 | H ₂ N- | 40 | H ₂ N- | 92 | 2,875 | 4,356 |
| 5 | O ₂ N- | 25 | 0 ₂ N- | 97 | 2,968 | 7,068 |
| 6 | Br | 35 | Br | 92 | 2,875 | 4,956 |
| 7 | ⟨_s↓_ı | 60 | | 89 | 2,781 | 2,781 |
| 8 | ⟨Br | 40 | | 92 | 2,875 | 4,356 |
| 9 | H ₃ C- | 45 | H ₃ C- | 90 | 2,812 | 3,749 |
| 10 | O ₂ NBr | 30 | 02N- | 94 | 2,937 | 5,875 |
| 11 | С | 2 h | CI | 70 | 2,187 | 1,093 |

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TABLE 2 Suzuki–Miyaura coupling reactions of aryl halides with PhB (OH)₂ catalyzed by MNC-Pd^a

Abbreviations: TON, turnover number (yield of product/per mol of Pd); TOF, turn over frequency (TON/time of reaction [h]).

 $^{\rm a}Reaction$ condition: aryl halide (1.0 mmol), phenyl boronic acid (1.2 mmol), K $_{\rm 2}CO_{\rm 3}$ (3 mmol), catalyst

(0.032 mol%), and EtOH/H2O (1/1; 5 ml) at 80°C.

^bIsolated yield.

temperature, the prepared catalyst was magnetically isolated with an outer magnet, and the product was extracted with ethyl acetate. Next, the organic layer was washed by water and dried with anhydrous MgSO₄. Copies of GC-FID chromatograms, ¹H NMR and ¹³CNMR of some selected products is available in supporting information.

3 | **RESULTS AND DISCUSSION**

The silk fibers can be transformed into N-doped carbon fibers with highly ordered graphitic structures during the heat treatment. Scheme 1 illustrates the structure of the pristine *B. mori* silk fibers and the transformation of silk fibroin molecular under heat



SCHEME 1 Procedure for preparation of MNC-Pd

treatment and the synthetic route used for the fabrication of the catalyst. The single silk fiber includes two parallel fibroin fibers, which are conglutinated by hydrophilic sericins. At molecular scale, silk fibroin comprises primarily hydrogen-bonded ß-sheet crystallites embedded in a less-ordered α -helix domain, leading to the exceptional strength and toughness of silk fibers. Under high temperature heat treatment (800°C) in the presence of KOH, as an active agent, the adjacent amide bonded protein chains can transform to aligned porous polyaromatic carbon structures (NC) due to intermolecular dehydration. After that, MNC was prepared according to a chemical coprecipitation procedure of FeCl₂.4H₂O and FeCl₃ 6H₂O in ammonia solution. Next, palladium nanoparticles were simply immobilized on the surface of MNC support in deionized water, the reduction of Pd (II) to Pd(0) was performed in the presence of NaBH₄. Finally, the catalyst was separated using a permanent magnet and dried under vacuum. The quantity of palladium on the surface of the MNC was measured using ICP-OES technique, and it was calculated to be 0.32 mmol g^{-1} . The predicted physicochemical features

of the magnetic catalyst were validated using FT-IR, TGA, EDX, SEM, TEM, XRD, and VSM techniques.

3.1 | Characterization of the catalyst

3.1.1 | FT-IR analysis

To characterize different functional groups presented in the structures of the NC and MNC-Pd nanoparticles, FT-IR spectroscopy was utilized. As shown in Figure 1a, there are three distinctive peaks at 3,444, 1,593, and $1,117 \text{ cm}^{-1}$ that could be attributed to the stretching vibrations of O-H and N-H, C=O and C=N, and C-OH, respectively.^[46] The existence of the O-H, C=O, and C-OH bonds can be attributed to the reaction of carbon with KOH during the activation process.^[47] FT-IR results suggest that the amide group nitrogen in silk undergo carbonization and form functional groups like N-H and C=N.

In addition, the band at 715 cm^{-1} is related to the substituted aromatic ring. There is a band located at 580 cm^{-1} which is more noticeable in the curve 1b rather



FIGURE 1 FT-IR spectrum of (a) NC and (b) MNC-Pd

than 1a, and it corresponds to Fe-O proving the existence of magnetite nanoparticles on the NC.

3.1.2 | SEM analysis

The surface morphology and structural changes resulting from the chemical modifications of NC, MNC, and MNC-Pd were recorded using SEM and TEM techniques presented in Figures 2 and 3, respectively. Based on previous report,^[48] the silk microfibers are essentially nonporous, judging from their smooth framework surface. After the carbonization via KOH activation at 800°C under N₂ atmosphere, the organic silk fibers convert into carbonized nitrogen-doped carbon fibers (NC), as shown in Figures 2a,b and 3a,b. There are many small pores randomly distributed across the surfaces. This indicated that the fibrous morphology could be well retained after the high temperature pyrolysis treatment. These pores derived from the thermal treatment process in the presence of KOH in which small molecule gases released and left spaces in the NC support. From the SEM and TEM images presented Figures 2c,d,e and 3c, it is evident that Pd and Fe₃O₄ nanostructures are uniformly dispersed on the surface of the synthesized NC support. In Figure 3c, Pd NPs can easily be recognized as it appears brighter than Fe₃O₄ NPs.

3.1.3 | EDX analysis

The EDX analysis was employed as a powerful technique to identify catalyst purity and the chemical composition of the synthesized MNC-Pd. The EDX spectrum proves the existence of expected elements comprising carbon, nitrogen, iron, oxygen, and palladium in the catalyst structure (Figure 4). The content of palladium obtained from EDX results is 3.4 wt% that is in good harmony with the ICP-OES analysis.

3.1.4 | VSM analysis

Magnetic property of MNC-Pd was measured using VSM technique at room temperature. According to Figure 5, the curve shows that the values of the saturation magnetization of MNC-Pd (37.98 emu/g) is below that of pure Fe_3O_4 nanoparticles (61.60 emu/g). It proves the existence of nonmagnetic compounds such as NC and Pd NPs in the catalyst. However, the catalyst could be swiftly and effectively removed from the reaction medium using an outer magnet.

3.1.5 | XRD analysis

Crystalline structure and the purity of the samples were investigated utilizing XRD analysis. The XRD patterns of NC, MNC, and MNC-Pd were displayed in Figure 6. Based on previous report,^[41] the silk fiber cocoon displays a main sharp peak at 19.6° that corresponds to the (020) diffraction peak of silk, exhibiting a typical β -sheet crystalline structure. After carbonization, the XRD pattern of NC shows a typical diffraction peaks located at 26.3° and 42.6° corresponding to (002) and (100) planes of hexagonal conjugated carbon structure (Figure 6a).^[22] The XRD pattern of MNC demonstrated in Figure 6b shows the bands corresponding to Fe₃O₄ structures. Six distinctive peaks are located at 2 θ = 30.86°, 36.26°, 43.15°, 53.81°, 57.19°, and 63.1°, which are related to **FIGURE 2** SEM of (a,b) NC, (c,d) MNC, and (e) MNC-Pd











(220), (311), (400), (422), (511), and (440) planes of the cubic magnetite with spinel structures, respectively (JCPDS 65-3107). Also, according to Figure 5c, existence of Pd(0) is proved $(2\Theta = 40.2^{\circ}, 46.7^{\circ}, 68.2^{\circ} \text{ and } 82^{\circ} \text{ that}$ related to (111), (200), (220), and (311)).^[49]

3.1.6 | TGA analysis

Thermal analysis of the synthesized NC and MNC-Pd was evaluated with thermogravimetric analysis within a range of 30°C-800°C under air flow at a heating rate of 10°C/min. The thermograms of NC and MNC-Pd are displayed in Figure 7. Based on previous report,^[24] the silk cocoon decomposes at about 300°C. The result of TGA of NC shows that it has very high thermal stability in comparison with the primary silk cocoon. Also, the prepared MNC-Pd shows high thermal stability as can be seen from Figure 6.

3.2 | Catalytic activity of MNC-Pd in Suzuki-Miyaura cross-coupling

C-C bond formation through Suzuki-Miyaura crosscoupling reaction was chosen to investigate the catalytic performance of the MNC-Pd (Scheme 2).

The reaction of iodobenzene and phenylboronic acid was chosen as a sample reaction to determine the optimal reaction conditions including the amount of catalyst, base and solvent type, and temperature. At first, the model reaction was conducted in different levels of MNC-Pd in H₂O at 80°C. It was found that the efficient amount of the catalyst is 0.032 mol% which provided a high yield within 30 min. Further increase in the catalyst amount did not raise the product efficiency or lessen the reaction time. Also, less catalyst amount lowered the reaction yield with longer reaction time. When the model reaction was carried out without catalyst, at 80°C, the desired product was not formed (Table 1, entries 1-6). To

Κα. 1100 1000 900 800 700 FeKa. 600 h Kα 500 The second secon ΝΚα 400 PdLβ 300 PdLa. el α. 200 FeKß 100 keV 0 ŝ 10 0





determine the optimal temperature, different temperatures were investigated for the model reaction, and it was found that the 80°C could afford the maximum efficiency (Table 1, entries 3, 7–9). Next, the solvent effect was investigated on the model reaction, and different solvents such as H_2O , DMF, CH_3COOEt , and EtOH were utilized to maximize the efficiency. A mixture of H_2O :EtOH in 1:1 ratio could afford the best result (Table 1, entries 3, 12–16). The efficacy of the base on the reaction was also checked. For this purpose, the sample reaction was accomplished in the presence of various bases such as K_2CO_3 , Na_2CO_3 , KOH, NaOH, and Et_3N , which K_2CO_3 was selected as the best base (Table 1, entries 12–15). Consequently, the most effective reaction medium was

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FIGURE 6 The XRD patterns of (a) NC, (b) MNC, and (c) MNC-Pd



FIGURE 7 TGA curves of (a) NC and (b) MNC-Pd

provided at 80°C using 0.032 mol% MNC-Pd and 3 mmol of K_2CO_3 in EtOH/H₂O (1/1) after 30 min (Table 1, entry 11).

Based on the obtained optimization results, the MNC-Pd was employed in the Suzuki–Miyaura reaction with various aryl halides including iodides, bromides, and chlorides. As shown in Table 1, all the precursors with electron-rich or electron-withdrawing substituents were successfully transformed to the desired products in high yields. Of the halogens, the order for activity of leaving group is as follows: Cl < Br < I; therefore, the results



SCHEME 2 Suzuki–Miyaura reaction catalyzed by MNC-Pd

founded from Table 2 are in consistent with predictions, and the reaction in the presence of aryl bromide and aryl chloride is slower than aryl iodides. MNC-Pd was insufficiently effective in aryl chloride reactions and longer reaction time was inevitable for increased performance. In addition, turnover frequency (TOF) and turnover numbers (TON) for all products included in Table 2 are calculated.

3.3 | Reaction mechanism

The proposed mechanism for the Suzuki–Miyaura crosscoupling reaction in the presence of MNC-Pd is shown in Scheme 3. Based on substrates chemistry together with some literature data, the possible mechanism has three steps. First step includes the oxidative addition of aryl halide to MNC-Pd which produces aryl palladium



SCHEME 3 Possible mechanism for Suzuki–Miyaura reaction catalyzed by MNC-Pd

TABLE 3 Comparison of MNC-Pd nanocomposite with other catalysts for the Suzuki-Miyaura cross-coupling reaction

| Entry | Catalyst | Condition | Time (min) | Yield (%) | Reference |
|-------|--|-----------------------------|------------|-----------|-----------|
| 1 | Pd-imino-Py-γ-Fe ₂ O ₃ | DMF, 100°C/ | 30 | 95 | [50] |
| 2 | GO/Fe ₃ O ₄ /PAMPS/Pd | EtOH:H ₂ O, 80°C | 120 | 100 | [51] |
| 3 | Pd@CC-SO3H-NH | H ₂ O, 100°C | 120 | 96 | [52] |
| 4 | Pd-ATBA-MNPs | 100°C/PEG | 40 | 97 | [53] |
| 5 | Pd/Fe ₃ O ₄ @SiO ₂ | EtOH, Reflux/MW | 30 | 99.7 | [54] |
| 6 | $[\kappa^3\text{-}N,N',\text{O-Pd}(1\subset 2)\text{H}_2\text{O}]\text{OAc}$ | H ₂ O, 25°C | 35 | 84 | [55] |
| 7 | Pd/CNFs | EtOH:H ₂ O, 80°C | 240 | 99 | [56] |
| 8 | MNC-Pd | EtOH: H_2O , 80°C | 30 | 97 | This work |

intermediate (I). Next phenylboronic acid which is activated by K_2CO_3 , reacts with intermediate (I), and in a transmetallation reaction, aryl palladium intermediate (II) is formed. Finally, the coupled product is generated by a reductive elimination of intermediate (II).

3.4 | Comparison of the catalytic activity of MNC-Pd with other reported catalysts

A catalytic performance comparison between the MNC-Pd nanocomposite and recently reported palladium catalysts is presented in Table 3. The new catalyst features easy synthesis process, magnetic separability, high stability, and great retrievability. Although the aforementioned catalysts in the previous papers have their own benefits, the newly prepared catalyst has significant potential in terms of reaction conditions containing products yield, temperature, reaction time, amount of catalyst, and separation. Considering the results, it can be found that MNC-Pd is an efficient catalyst, and it is beneficial in the synthesizing of biaryl compounds via Suzuki–Miyaura coupling reaction.

3.5 | Recycling of the catalyst

The catalyst reusability is an important factor for commercial and industrial applications. For this purpose, after the first run, the catalyst was isolated by an outer magnet and then washed with ethanol followed by drying

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FIGURE 9 EDX spectra of the recovered MNC-Pd after being reused six times



FIGURE 10 Leaching experiment of MNC-Pd

at 80°C under vacuum conditions. Next, the separated, used catalyst was again added to a reaction vessel containing starting materials. The reaction was carried out for six cycles, and the results have been presented in Figure 8. The catalyst could be used for six cycles without significant loss in its performance. Furthermore, EDX technique was used to evaluate the changes in the elemental composition of the used MNC-Pd. As shown in Figure 9, the palladium content which was leached after six cycles was insignificant. To study the leaching of Palladium, ICP-OES analysis of the recovered catalyst was also carried out. According to the achieved results, no appreciable decrease in the Pd content was observed. The Pd amount in the primary catalyst and the reused catalyst was 0.32 and 0.29 mmol/g, respectively, that demonstrated the Pd-leaching of the catalyst is negligible.

3.6 | Leaching

In another investigation to determine the leaching of palladium from the MNC-Pd, once 15 min of the reaction time passed, the catalyst was separated from the reaction medium. The remaining mixture was kept to continue the reaction under optimized conditions. According to Figure 10, a very slight increase was observed even after 40 min. The results proved the real heterogeneous nature of the catalyst.

4 | CONCLUSION

In summary, natural silk cocoons were used to make new a nitrogen-doped carbon material by thermal treatment for catalytic purposes. In fact, the combination of Fe_3O_4 nanoparticles with the new nitrogen-doped carbon material created a good support for palladium to form MNC-Pd. The new catalyst offers several advantages including biodegradability, biocompatibility, and efficient magnetic separation. The results proved excellent catalytic performance in Suzuki cross-coupling reaction. Further, the catalyst can be employed for six consecutive cycles without any considerable loss in its efficiency. Both fabrication and application of MNC-Pd can be considered a green approach because both follow green chemistry principles. Further investigations are underway to expand the application nitrogen-doped carbon materials derived from silk cocoons for catalytic purposes in our research team.

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AUTHOR CONTRIBUTIONS

Parisa Akbarzadeh: Conceptualization; data curation; formal analysis; funding acquisition; investigation; methodology; project administration; resources; software; supervision; validation; visualization.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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