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#### RESEARCH ARTICLE



## A comparative study of catalytic activity on iron-based carbon nanostructured catalysts with Pd loading: Using the Box–Behnken design (BBD) method in the Suzuki–Miyaura coupling

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#### Abstract

Highly dispersed palladium nanoparticles immobilized on surface-modified Fe<sub>3</sub>O<sub>4</sub> NPs and magnetic carbon nanostructures (CNSs; carbon nanotubes/ graphene oxide) were synthesized and applied as a recyclable and reusable nanocatalyst to achieve palladium (II)-catalyzed Suzuki-Miyaura reaction of arylboronic acid with aryl bromides. Carbon nanostructures with immobilized hydantoin (PH)-Pd complex display excellent stability, including a high performance at low catalyst loading. Magnetic separation prevents catalyst centrifuge or filtration and also contributes to practical techniques for recovery. Next, a response surface method based on a three-level Box-Behnken design was used, which involved three factors: catalyst loading, reaction time, and solvent. The Box-Behnken method was advantageous to parameters optimization for obtaining a yield, with high efficiency and accuracy. As a result of catalytic tests, the TONs and TOFs were calculated from all coupling reactions. The prepared nano-magnetic catalysts, after the catalysis reaction, can be easily recovered through the magnetic field. Evaluated catalytic performance indicates that these types of catalysts can function as effective recyclable catalysts at least five times without losing the initial level of catalytic activity.

#### **KEYWORDS**

Box–Behnken design (BBD), carbon nanostructures (CNSs), Fe<sub>3</sub>O<sub>4</sub>-NPs, nano-magnetic catalyst, Suzuki–Miyaura Coupling

## **1** | INTRODUCTION

For more than 30 years, Pd-catalyzed homogeneous bonding reactions have been used in C–C coupling reactions such as Heck, Sonogashira, Suzuki, Kumada, Negishi, Hiyama, and so forth.<sup>[1–4]</sup> These catalysts have limitations that hampered their industrial applications, and the constraints include high expense, non-recyclability, and challenges in removal from the products.<sup>[5]</sup> To overcome such limitations, coupling reactions catalyzed

by solid-supported Pd as a heterogeneous catalyst have received much attention. Among the solid supports used in constructing heterogeneous catalysts, carbon nanostructures (CNSs) are more popular due to their high thermal resistance, chemical stability, and large surface.<sup>[6–10]</sup> Recently, research has focused on nano-sized carbon materials such as graphene oxide (GO) and carbon nanotubes (CNTs) to achieve their unique properties.<sup>[11]</sup> GO has been considered as a support for catalytic activities due to its unique properties such as high surface

area, superior chemical stability, two-dimensional (2D) structures, and low cost.<sup>[12-14]</sup> In addition, GO contains many functional groups such as hydroxyl, carbonyl, and epoxy, which cause these hydrophilic groups to quickly disperse in water and form a stable colloidal suspension.<sup>[15–17]</sup> Although GO has been studied extensively in this field,<sup>[18-20]</sup> CNTs have also been used as solid support for catalytic activity in recent years.<sup>[21,22]</sup> CNTs behave as rolled cylinders of graphene sheets.<sup>[23]</sup> Multiwall carbon nanotubes (MWCNTs) have exceptional properties such as structural and thermal stability and also insolubility in most solvents. They are easily functionalized and are suitable support for immobilizing catalytic species.<sup>[24-26]</sup> An issue in using a CNS immobilized combination is their recovery from the reaction mixture for repeated use. Recycling these catalysts requires a tedious centrifugation process. Due to their small size, recycling from the reaction solution is difficult and leads to a significant reduction in their catalytic activity. A practical solution is to immobilize the surface of carbon nanostructures with magnetic iron oxide nanoparticles (IONPs).<sup>[27,28]</sup> With the development of nanoscience, the combination of magnetic nanoparticles and different nanomaterials has become possible to prepare a multifunctional magnetic nanocatalyst with excellent catalytic properties.<sup>[29,30]</sup> Magnetic nanoparticles (MNPs) with their unique magnetic properties have potential applications in drug delivery, biological systems, and catalysis reactions.<sup>[31-33]</sup> Here, a combination of magnetic nanoparticles (Fe<sub>3</sub>O<sub>4</sub>) as magnetically recoverable catalysts promises a solution to overcome the above drawbacks by providing an active surface for adsorption and immobilization of ligands and metal.<sup>[34–36]</sup> It is clear that homogeneous catalysts have higher catalytic activity than their heterogeneous counterparts, but expensive metal catalysts are difficult to recycle and lead to waste production and contamination of products.<sup>[37,38]</sup> Therefore, as is evident, recyclability and reusability performance are significant parameters to develop economic processes.<sup>[39-42]</sup> Metal nanocatalysts can be stabilized either by chemical adsorption of presynthesized metal nanoparticles or by direct growth of magnetic nanoparticles using grafted organic functional molecules on the support.<sup>[43-46]</sup> The results of Crooks and Christensen groups showed high catalytic activity of the nano-magnetic catalyst for reactions such as Suzuki, hacking, hydrogenation, and so forth.<sup>[47-49]</sup> For this purpose, hydantoin ligand and terminal amino groups were considered to graft from the Fe<sub>3</sub>O<sub>4</sub> supports. Glycolylurea, also known as hydantoin, is a heterocyclic organic compound with the formula  $CH_2C(O)NHC(O)$ NH, which was discovered in 1861 by the reduction or hydrogenation of allantoin by Baeyer.<sup>[50]</sup> Hydantoin groups have many applications, including in medicine, textile printing, catalysts, and the production of resins and plastics.<sup>[51–55]</sup> In this paper, we design and synthesize several iron-based nanostructured catalysts. Among Pdcatalyzed cross-coupling reactions, the reaction of organohalides with organoboronic acids (Suzuki) has proven to be a very popular and versatile method for the formation of carbon-carbon bonding.<sup>[56,57]</sup> Suzuki-Miyaura reactions are environmentally benign, have a high tolerance to different functional groups, are easily available, have high stability of used substrates, and are widely used to form natural products, biologically active pharmaceuticals, and agrochemicals.<sup>[58,59]</sup> Based on this, we decided to evaluate and compare the catalytic activity of magnetic nanocatalysts synthesized by Suzuki-Miyaura cross-coupling reactions. These nanocomposites showed high catalytic activity in the C-C cross-coupling reaction.

However, these catalytic reactions are associated with a new set of optimization problems. Statistical Design of Experiments (DoE) is a handy tool and a powerful approach to identify and optimize the relevant process conditions.<sup>[60]</sup> Amongst the 12 known principles of green chemistry, fewer solvents and reagents are used to provide less chemical waste, and DoE increases the application of green chemistry principles. Therefore, DoE has provided the ability to enable scientists to accept optimal response conditions more widely. The traditional optimization approach has many drawbacks varying one variable at a time (OVAT). DoE is a tool for solving optimization problems promptly. The reasons are that, first, the outcomes are highly dependent on the starting point. It rarely reveals optimal conditions for the most part. Second, the OVAT approach is laborious and timeconsuming, requires many raw materials, and only looks at one factor at a time, unable to detect factor interactions. Third, the OVAT approach is not able to separate the "noise" (the inherent run-to-run variation of a system) from a real recovery reaction, unless a large number of responses are repeated using the same conditions.<sup>[61]</sup> Therefore, the barriers to the OVAT approach in optimizing reactions lead to the broader use of DoE in optimizing chemical reactions. Also, we recorded excellent turnover number (TON) and frequency (TOF) values for the catalyst with very low catalyst loading. Overall, these nano-magnetic catalysts show promising results on sensitivity, repeatability, and stability.

## 2 | RESULT AND DISCUSSION

In this study, iron-based nanostructures catalysts Pd-PH@CSMNPs, Pd-PH@CNT-CSMNPs, and Pd-PH@GO- CSMNPs were successfully synthesized. Then their catalytic activity was compared with optimize the Suzuki-Miyaura cross-coupling reaction in the statistical DoE approach. In order to magnetically synthesize CNS, graphite and multi-walled carbon nanotubes were first oxidized to increase activity by a reported procedure.<sup>[35,62]</sup> After reacting with Fe<sub>3</sub>O<sub>4</sub> nanoparticles to obtain a negative charge surface, we coated them with a thin layer of SiO<sub>2</sub>. Then hydantoin ligand (PH) was immobilized onto the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> surface by the covalent bond. Later, the palladium nanoparticles were immobilized on the surfaces of PH-coated Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>, based on the formation of Pd<sup>II</sup> nanoparticles. In the next step, this nano-magnet catalytic was synthesized based on CNSs (carbon nanotubes [CNTs] and graphene oxide [GO]). The advantage of the nanocomposites synthesized Applied Organometallic\_WILEY<sup>3 of 20</sup> Chemistry

by this method is the easy and suitable reaction conditions. They can also be separated from the reaction system in a short time by using a magnetic field. Therefore, they can be used repeatedly without significant reduction in catalytic activity. A schematic illustration of the preparation process of Pd-PH@CSMNPs, Pd-PH@CNT-CSMNPs, and Pd-PH@GO-CSMNPs nano-magnetic catalysts is shown in Scheme 1.

# 2.1 | Characterization of nano-magnetic catalysts

In this paper, nano-magnetic catalysts are characterized by Fourier-transform infrared (FT-IR), X-ray powder diffraction (XRD), energy-dispersive spectroscopy (EDS),



**SCHEME 1** Schematic of synthesis of (a) Pd-PH@CSMNPs and (b) Pd-PH@CNS-CSMNPs Nano-magnetic catalysts -WILEY Chemistry

#### 2.1.1 | NMR analysis

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The <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra of the hydantoin ligand confirmed the synthesizing and for the <sup>1</sup>H NMR showing the signals of the aromatic, NH(1) and NH(2) at 7.38–8.68, 9.54, and 11.33 ppm, respectively. Also, <sup>13</sup>C NMR of hydantoin ligand demonstrated a chemical shift in the regions of 69.4, 121.9–149.6, 155.8, and 173.5 ppm, which are attributed to the groups of C(5), aromatic rings, CO(1), and CO(2), respectively (see Figures S1 and S2 in the Supporting Information).

#### 2.1.2 | FT-IR analysis

The nano-magnetic catalysts were characterized by FT-IR spectra to confirm the successful attachment. After oxidation of carbon nanostructures (CNTs and GO) by mixed acid solution ( $H_2SO_4/HNO_3$ ), the CNSs surface contains many oxygen-containing active groups such as  $-COO_-$ ,

-OH, and -C=O. These active groups act as the nucleation sites of iron oxide nanoparticles. The presence of iron oxide nanoparticles also leads to a reduction in oxygen-containing groups during the reaction, which can be confirmed using FT-IR spectroscopy. Figure 1 shows the FT-IR spectra of oxidized MWCNTs, Pd-PH@CNT-CSMNPs, GO, Pd-PH@GO-CSMNPs, Pd-PH@CSMNPs, and PH.

The FT-IR spectra of the products were recorded at each step of the synthesis of the nano-magnetic catalysts to investigate the production of the expected products. The FT-IR spectrum of oxidized MWCNTs is displayed in Figure 1a that the absorption bands at  $3422 \text{ cm}^{-1}$  (which is assigned to the stretching vibration of OH groups) and  $1720 \text{ cm}^{-1}$  (corresponding to the C=O vibrations) shows the presence of functional groups (COOH) on the surface of the MWCNTs. As can be seen in Figure 1c, the FT-IR spectrum of GO represents a broad peak at 3415 cm<sup>-1</sup> as well as another one at  $1720 \text{ cm}^{-1}$ , which is attributed to the stretching vibrations of the OH and C=O groups, respectively. The FT-IR spectrum of hydantoin ligand (PH) is shown in Figure 1f. Figure 1b,d,e shows the FT-IR spectra of hybrid magnetic nanoparticles, Pd-PH@CNT-CSMNPs, Pd-PH@GO-CSMNPs, and Pd-PH@CSMNPs, respectively.

Previous work has shown that FT-IR spectra of magnetite, which has two strong infrared absorption bands at  $570 \text{ cm}^{-1}$  and  $390 \text{ cm}^{-1}$ , can be attributed to the Fe–O



**FIGURE 1** FT-IR spectra of (a) oxidized MWCNTs, (b) Pd-PH@CNT-CSMNPs, (c) GO, (d) Pd-PH@GO-CSMNPs, (e) Pd-PH@CSMNPs, and (f) PH

stretching, thus confirming the presence of  $Fe_3O_4$  in the samples.<sup>[63]</sup> The absorption bands at 1210, 1087, 947, and  $473 \text{ cm}^{-1}$  were also ascribed to the stretching vibrations of SiO<sub>2</sub>, indicating the coating of the silica shell on the magnetite surface. Based on the spectra, the C-Cl peaks are removed after binding the hydantoin ligand. According to the spectra, the stretching vibration of the C=O group decreased, and starching vibration of the C-N and C=N groups ( $\sim$ 1331 and  $\sim$ 1653 cm<sup>-1</sup>) appeared after hydantoin ligand bonding on the surface of the nanocatalysts. The peak at  $1720 \text{ cm}^{-1}$ , corresponding to the hydantoin cycle, shifted towards lower wavenumbers after the metal bonds in the magnetic nanocatalyst. This adsorption peak is observed at 1657 cm<sup>-1</sup>, which confirms that palladium chloride is successfully anchored onto the surface of nanocomposites. A comparison of the IR spectra mentioned above indicates the successful combination of nanocatalysts.

## 2.1.3 | FE-SEM analysis

Scanning electron microscopy (SEM) was investigated to reveal the morphological properties of the nanocatalysts. Figure 2 shows the SEM images of samples Pd-PH@CNT-CSMNPs, GO, Pd-PH@GO-CSMNPs, and Pd-PH@CSMNPs.

The presence of spherical  $Fe_3O_4$  NPs, with diameters up to ~40 nm, was confirmed in each sample. The SEM image in Figure 2a is an indication that the CNTs are uniformly filled with magnetic iron oxide ( $Fe_3O_4$ ) nanoparticles. These images confirm our method for large-scale CNTs filling with  $Fe_3O_4$  nanoparticles and also maintains the filling process of the CNTs backbone mechanical integrity. At the edges of CNTs (for example, the red circle in Figure 2b), the brightness is higher than in other areas because these areas have much more oxygen-containing groups that can facilitate the



**FIGURE 2** SEM images in several different magnifications of Pd-PH@CNT-CSMNPs (a-c), GO (d), Pd-PH@GO-CSMNPs (e, f), and Pd-PH@CSMNPs (g-i)

accumulation of Fe<sub>3</sub>O<sub>4</sub> nanoparticles. Scanning electron microscopy (SEM) images of (Pd-PH@CNT-CSMNPs) showed the presence of CNTs filaments of average diameter ~49 nm (Figure 2c). It is observed that the mean diameter (Pd-PH@CNT-CSMNPs) is higher than pristine MWCNTs.<sup>[64]</sup>

Figure 2d shows the SEM image of pure GO. The SEM image of Pd-PH@GO-CSMNPs (Figure 2e,f) displayed the  $Fe_3O_4$  NPs coverage over the surface of the nano-magnetic catalyst. The presence of abundant oxygen at the surface and edges might provide additional sites that enable high iron nanoparticle loading. Figure 2g–i shows the nanoparticle size and typical SEM image of Pd-PH@CSMNPs. As shown in the picture, most of the prepared NPs are spherical-shaped and their average diameter is about 20–30 nm.

## 2.1.4 | XRD analysis

The phase composition and crystallographic structure of MWCNT, Pd-PH@CNT-CSMNPs, GO, Pd-PH@GO-CSMNPs, and Pd-PH@CSMNPs composites are determined by X-ray powder diffraction (XRD), as shown in Figure 3.

The peaks  $2\theta = 26.5^{\circ}$  and  $40.6^{\circ}$  in MWCNT can be attributed to (002) and (110) CNTs planes. The diffraction peak at 40.6° confirms the multi-walled structure of carbon nanotubes. The X-ray diffraction pattern of GO

showed the characteristic peak at  $2\theta = 10^{\circ}$ , which confirms the synthesis of the sample of GO. The XRD spectrum of the synthesized samples Pd-PH@CNT-CSMNPs, Pd-PH@GO-CSMNPs, and Pd-PH@CSMNPs show a formation of Fe<sub>3</sub>O<sub>4</sub> nanoparticles, which is consistent with previous reports.<sup>[65]</sup>

Relatively sharp diffraction peaks indicate that  $Fe_3O_4$ nanoparticles have relatively high crystallization. The XRD pattern of the synthesized nanocomposite (Pd-PH@CNT-CSMNPs) and (Pd-PH@GO-CSMNPs) shows a peak attributable to the carbon phase CNTs and GO, respectively. The peak regions and relative intensities are consistent with XRD standard data (JCPDS no. 19-0629), and the presence peaks at 18.46°, 30.66°, 35.85°, 43.64°, 53.95°, 57.40°, and 63.08° are associated with the (111), (220), (311), (400), (422), (511), and (440) crystal planes of Fe<sub>3</sub>O<sub>4</sub>, respectively (see Table S1). The absence of any additional peaks belonging to the other phases indicates good crystallization and high purity of the nano-magnetic catalysts.

#### 2.1.5 | EDS analysis

To confirm the synthesis of the nano-magnetic catalysts, energy dispersive spectroscopy (EDS) was measured for the prepared catalysts PH@CNT-CSMNPs, PH@GO-CSMNPs, and PH@CSMNPs, as shown in Figure 4.



FIGURE 3 The XRD patterns of GO, MWCNT, Pd-PH@GO-CSMNPs, Pd-PH@CSMNPs, and Pd-PH@CNT-CSMNPs

**FIGURE 4** EDS analysis for elemental composition of PH@GO-CSMNPs (a), PH@CNT-CSMNPs (b), and Pd-PH@CSMNPs (c) nano-magnetic catalysts



FIGURE 5 (a) Magnetization curves of Pd-PH@CNT-CSMNPs, Pd-PH@CSMNPs, and Pd-PH@GO-CSMNPs samples; (b) photograph of nano-magnetic catalyst (Pd-PH@GO-CSMNPs) dispersed in ethanol (right) and its response to a magnet (left)

applied field (Oe)

The EDS spectra of the nanocomposites revealed the presence of C, O, N, Cl, Si, Fe, and Pd elements, which the elements of Fe arise from  $Fe_3O_4$ , the element of Si arises from  $SiO_2$ , the elements of Pd arise from the Pd nanoparticles, and the C and O mainly come from hydantoin ligand (PH) and some oxygen-containing functional groups of CNTs and GO (Figure 4a–c). It confirms the presence of magnetic nanoparticles (MNPs), PH, and PdCl2 groups on the surface of CNSs.

Additionally, the Pd loading of the nanocatalysts was confirmed by measuring the weight percentage of the palladium in the samples by the ICP-OES analysis. The amount of Pd on the supports was determined as 19.11%, 21.45%, and 14.15% for Pd-PH@CNT-CSMNPs, Pd-PH@GO-CSMNPs, and Pd-PH@CSMNPs Respectively. As we expected, the ICP-OES and EDS measurements for nano-magnetic catalysts also proved the presence of Pd nanoparticles.



#### 2.1.6 | VSM analysis

Figure 5a shows the magnetic performance of Pd-PH@CNT-CSMNPs, Pd-PH@GO-CSMNPs, and Pd-PH@CSMNPs samples by VSM analyzer at room temperature. Magnetic curves showed that all samples were superparamagnetic at room temperature.

The saturation magnetization values for Pd-PH@CSMNPs, Pd-PH@GO-CSMNPs, and Pd-PH@CNT-CSMNPs were 27.13, 31.72, and 42.1 emu  $g^{-1}$ , respectively. The results showed that with the increase of carbon nanostructures, the magnetization of hybrids is significantly reduced. These behaviors indicate that the synthesized samples exhibit a superparamagnetic behavior due to the presence of ultra-small Fe<sub>3</sub>O<sub>4</sub> NPs. However, magnetic nanocatalysts can be removed from the solution in 10 s using a supermagnet. To investigate the colloid stability of the composite materials, the synthesized samples can be easily dispersed in ethanol and can be highly stable at room temperature for at least 6 months. These nano-magnetic catalysts can be quickly separated from the solution by holding the sample near a commercial magnet, as shown in Figure 5b. They also disperse quickly as soon as the magnet is removed.

#### 2.1.7 | TEM and histogram analysis

To further illustrate the successful functionalization of the synthesized nano-magnetic catalysts, transmission electron microscopy (TEM) was performed. Figure 6a,c,e shows the TEM micrographs of the Pd-PH@CNT-CSMNPs, Pd-PH@GO-CSMNPs, and Pd-PH@CSMNPs samples, respectively.

Identification of the heterogeneous surface with the random distribution of Fe<sub>3</sub>O<sub>4</sub> was possible by forming small spheres of MNPs.Also, the particle size can be explained through histogram diagrams. Histogram diagrams of all three samples are given in Figure 6b,d,f. Because smaller nanoparticles cause more dispersion, the more excellent dispersion of these active sites directly affects the catalytic activity.<sup>[66]</sup> The obtained particle size distribution histogram showed that the particle size was in the range of 10–70 nm, and the majority of particles (70–65%) were in the range of  $\sim$ 25–35 nm.



FIGURE 6 TEM micrograph and histogram of the particle size distribution for Pd-PH@CNT-CSMNPs (a and b), Pd-PH@GO-CSMNPs (c and d), and Pd-PH@CSMNPs (e and f) samples

## 2.1.8 | TGA analysis

The thermal stability of Pd-PH@CNT-CSMNPs, Pd-PH@GO-CSMNPs, and Pd-PH@CSMNPs samples was investigated via thermogravimetric analysis (TGA), as shown in Figure 7.

Thermal gravimetric analysis showed a successful grafting of  $Fe_3O_4$  NPs on the supporting surface by increasing the thermal stability of these nanocomposites compared with their nanocarbon structures.<sup>[67,68]</sup> The residual weight at 600°C for Pd-PH@CNT-CSMNPs was about 84.81 wt% and for Pd-PH@GO-CSMNPs was about 71.72 wt% as compared with the Pd-PH@CSMNPs with



FIGURE 7 TGA curves of Pd-PH@CSMNPs, Pd-PH@GO-CSMNPs, and Pd-PH@CNT-CSMNPs nanocomposites

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95.67 wt% (Figure 7). For the Pd-PH@CSMNPs nanoparticles, the main weight loss occurred above 700°C due to the lack of significant organic components. However, this sample had much higher thermal stability rather than both Pd-PH@GO-CSMNPs and Pd-PH@CNT-CSMNPs. The highest weight loss is observed above 210°C, which can be attributed to the breakdown of the CONHPd groups conjugated with Fe<sub>3</sub>O<sub>4</sub> nanoparticles of the Pd-PH@CSMNPs nanocomposite. The thermogram of Pd-PH@CNT-CSMNPs showed two main stages of weight losses a 3% of weight loss at 300°C and 7% above 500°C. The initial losses are attributed to the decomposition of labile oxygen deriving from functional groups and organic components, and the removal of most of the stable functionalities deriving from Fe<sub>3</sub>O<sub>4</sub> NPs. The TGA curve of Pd-PH@GO-CSMNPs nanocomposite showed a profile similar to Pd-PH@CNT-CSMNPs, although it revealed a difference of weight loss of 14% in comparison to the Pd-PH@CNT-CSMNPs system in the temperature range 400-600°C.

## 2.1.9 | Elemental mapping analysis

To investigate the uniformity of the elements, the elemental mapping of catalyst Pd-PH@GO-CSMNPs was examined (Figure 8a–i). These figures clearly show that



FIGURE 8 The corresponding elemental mapping pattern of Pd-PH@GO-CSMNPs nano-magnetic catalyst (a–i)

all the elements are dispersed uniformly on the surface of the functionalized graphene oxide.

## 2.2 | Optimization of reaction for Suzuki coupling reactions using design of experiments (DoE) method

In recent decades, carbon-carbon bonding reactions have received widespread attention as a powerful and useful tool for the synthesis of organic compounds. Suzuki-Miyaura cross-coupling reactions are one of the most widely used coupling reactions. The controversial issue in the chemical industry is the toxicity and high cost of palladium metal. For this reason, heterogeneous and magnetic catalysts have been considered due to the easy recovery of the reaction mixture and the possibility of reuse. Current research is directed towards increasing the efficiency of these catalysts. For this purpose, the catalytic activity of three synthesized nano-magnetic catalysts in the Suzuki-Miyaura cross-coupling reactions was investigated and compared.In this study, we report using the DoE technique to minimize experimentation processes and optimize the gathered data. A large number of parameters studied, such as catalyst, solvent, and time, suggested a DoE approach. To begin the study of catalytic activity, we need a model reaction using the couplings of phenylboronic acid with bromobenzene. In the beginning, the Pd-PH@CSMNPs (catalyst 1), Pd-PH@CNT-CSMNPs (catalyst 2), and Pd-PH@GO-CSMNPs (catalyst 3) were selected as the catalyst. The amount of solvent is the second important parameter. According to previously published reports, the most common solvent for the Suzuki-Miawara connection is dimethylformamide (DMF).<sup>[69]</sup> Another influential factor is the reaction time. So, three main factors that can affect the yield of the

reaction are the amount of solvent (A), catalyst (B), and time (C), while the response of interest (dependent variable) is the yield of the reaction. These three variables have the most significant impact on production. Box-Behnken experimental design was used to evaluate the effect of each variable.<sup>[70,71]</sup> The response level results were analyzed based on the percentage of efficiency to determine the optimal conditions using DMF solvent with nano-magnetic catalyst. We began our investigation of the cross-coupling reaction using bromobenzene as the electrophile and phenylboronic acid as the nucleophile. A list of the variables examined and the level of dependent responses is depicted in Table 1.

Accordingly, the amount of solvent ranged from 5 to 20 ml, catalyst loading ranged from 0.005-0.01 mol%, and reaction time ranged from 1 to 3 h. In our study, the Box-Behnken design (BBD) was applied with three factors at three levels, with three center points, one response (yield%), and a total of 15 experiments. Design-Expert Software (Version 11, Stat-Ease, Inc., Minneapolis, MN 55413) was applied for data analysis. Our target is to maximize the final yield of the Suzuki-Miyaura reaction compounds. In general, it has been proven that the catalytic efficiency of these nano-magnetic catalysts is very high and the Suzuki corresponding product has been obtained with high purity in most reactions. A comparison of the efficiency of catalysts 1, 2, and 3, which catalyze the Suzuki C-C coupling reactions under the same conditions, is also shown in Figure 9.

Among the presented catalysts, Catalyst **1** has no carbon structure and shows lower efficiency. On the other hand, catalysts with carbon nanotube and graphene carbon structures led to higher yields in catalysts **2** and **3**. These results suggest that the addition of carbon structures to metals with catalytic properties, such as palladium, increases the catalytic properties. Also, by

TABLE 1	The levels of independent variables examined, the unit, and the range of dependent response of the biphenyl production using
Box-Behnker	design

$X - (Ar) + (HO)_2 B - (Ar) -$					
Variable	Factor coding	Unit	low level (-1)	0	high level (+1)
Solvent	А	ml	5	12.5	20
Catalyst (1, 2, and 3)	В	mol%	0.005	0.0075	0.01
Reaction time	С	hour	1	2	3

FIGURE 9

Applied Organometallic\_ Chemistry 11 of 20 WILEY 100 90 80 70 % Conversion Catalyst 2 60 50 Catalyst 3 40 30 20 10 0 2 3 5 6 7 8 10 11 12 13 14 15 4 Run

catalysts 1, 2, and 3 by coupling bromobenzene and phenylboronic acid, by optimizing the conditions with the Box–Behnken method for phenylboronic acid (1 mmol), bromobenzene (0.75 mmol), catalyst ( $7.5 \times 10^{-3}$  mol%), DMF, 130°C, 2 h

Comparative catalytic study for

TABLE 2 Box-Behnken design conditions for optimizing the biphenyl production with corresponding experimental results

Variables	Solvent	Catalyst	Time	Yield catalyst 3
(unit)	(DMF)	(mol%)	(hour)	
Run	A	B	c	(%)
1	20	0.0075	1	82
2	5	0.005	2	77
3	5	0.0075	3	45
4	12.5	0.0075	2	92
5	12.5	0.01	1	86
6	20	0.01	2	77
7	5	0.0075	1	65
8	20	0.005	2	83
9	12.5	0.005	1	76
10	12.5	0.0075	2	86
11	5	0.01	2	55
12	12.5	0.01	3	54
13	12.5	0.0075	2	84
14	12.5	0.005	3	87
15	20	0.0075	3	67

increasing the catalytic activity of **3** compared with **2**, it was found that the smaller size of the nanoparticles and the larger surface area increase the catalytic activity and greater efficiency. Therefore, nano-magnetic catalyst **3** was chosen as a proper catalyst with high yield activity toward the Suzuki cross-coupling reaction (see Table S2). Yield in the design space ranged from 45% to 92%, and curvature was detected from yield at the center point conditions. Therefore DoE was carried out, using response surface methodology (RSM). Table 2 summarizes the results of the relevant tests.

Table 3 shows the p value of the term type (which was significantly less than 0.05), along with the analysis of variance (ANOVA) summary of the RSM.

Figure 10a,b shows the normal plot of residuals and predicted versus actual plots comparing the experimental values with the predicted values for model evaluation. The plots show a minor deviation from the line, between the actual and predicted values and the normal plot of residuals, which determines the accuracy of the model prediction.

Two-dimensional contour graphs and three dimensions surface plots were used to analyze the combined effect of factors on efficiency. Figures 11, 12, and 13 show the response surface curves and contour plots for yield and the three independent variables. The effect and interaction of each of the independent variables were examined. The response surfaces displayed an exact peak point

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#### TABLE 3 Analysis of variance (ANOVA) of the experimental result of the BBD

Source	Sum of squares	df	Mean square	F value	p value	
Model	2700.18	9	300.02	19.38	0.0023	significant
A-Solvent	561.12	1	561.12	36.24	0.0018	
<b>B-Catalyst</b>	325.13	1	325.13	21.00	0.0059	
C-Time	392.00	1	392.00	25.32	0.0040	
AB	64.00	1	64.00	4.13	0.0977	
AC	6.25	1	6.25	0.4037	0.5531	
BC	462.25	1	462.25	29.85	0.0028	
$A^2$	592.41	1	592.41	38.26	0.0016	
B <sup>2</sup>	10.26	1	10.26	0.6624	0.4527	
$C^2$	363.10	1	363.10	23.45	0.0047	
Residual	77.42	5	15.48			
Lack of fit	42.75	3	14.25	0.8221	0.5897	not significant
Pure error	34.67	2	17.33			
Cor total	2777.60	14				



**FIGURE 10** Graphical plot of normal plot of residuals (a) predicted versus actual values (b)

**FIGURE 11** (a) Response surface curve and (b) contour plot. The response surface plot and contour plot of the yield biphenyl (%) for the interaction effects solvent with time

that revealed the optimum condition and the highest yield in product production, which were achieved inside the design boundary area for all three variables. Solvent (A) interaction in the range of 5 to 20 and reaction time (C) from 1 to 3 h at constant Pd-PH@GO-CSMNPs catalyst amount (B) of 0.0075 mol% at the response surface shown in Figure 11a is provided. It is observed that the highest yield is produced with 12.5 ml of solvent and 2 h



reaction time. In the contour plot of the conversion response model in Figure 11b, from front to back, with color code changing from blue to red, the contour lines indicate that the yield of biphenyl is above 60%, 70%, and 80%, respectively. The yield increased due to the increasing amount of solvent. Yield increased with more solvent, but with excess solvent, the performance began to decrease.

The response surface illustrated in Figure 12a represents the interaction effect when the Pd-PH@GO-CSMNPs catalyst amount (B) was varied from 0.01 to 0.005 mol% and reaction time (C) was increased from 1 to 3 h at a constant solvent (A) of 12.5 ml. The highest yield percentage can be seen in the 0.0075 mol% of catalyst and 2-h reaction time. As the amount of catalyst increases, the reaction's efficiency increases, but from a specific value onwards, increasing the catalyst does not have a significant effect on increasing product efficiency, so a small amount is preferred due to the high cost of the catalyst. Furthermore, in the contour plot of the yield response model in Figure 12b, from back to front, with color code changing from green to orange-red, the contour lines indicate that the efficiency is above 60%, 70%, 80%, and 90%, respectively.

The response surface shown in Figure 13a describes the interaction influence of solvent (A) from 5 to 20, and Pd-PH@GO-CSMNPs catalyst amount (B) from 0.01 to 0.005 mol% at a constant reaction time (C) of 2 h. As can be seen, the highest yield percentage was produced in a 12.5-ml solvent and 0.0075 mol% catalyst. As the solvent increased, the yield also increased. By adding more solvent, the yield increased steadily, but when the amount exceeded 12.5 ml, the excess solvent reduced the yield. Less use of the catalyst also increases the percentage of vield, and additional catalysts reduce the percentage of the product (contour plot in Figure 13b).

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Therefore, the optimum point of the design involves a 12.5-ml solvent, 0.0075 mol% of Pd-PH@GO-CSMNPs catalyst, furthermore a 2-h reaction time. Optimal conditions lead to the maximum predicted yield value of 92%.

#### The substrate scope of reactions 2.3 Suzuki-Miyaura cross-coupling

With the optimized conditions obtained for the crosscoupling reactions with catalyst 3, we then investigated the substrate scope (Table 4).



## **TABLE 4** Suzuki coupling reactions of various aryl bromides and arylboronic acid over catalyst **3**<sup>a</sup>

	(HO) <sub>2</sub> B- R <sub>2</sub> = CHO COM	$ \begin{array}{c} & & \\ & & \\ & & \\ & \\ & \\ & \\ & \\ & \\ $			
Aryl bromide	R <sub>2</sub>	Product	Yield <sup>b</sup> (%)	TON <sup>c</sup>	TOF <sup>d</sup> (h <sup>1-</sup> )
Br	-H		92	12,267	6133
1	-COMe	Ia Me	91	12,133	6066
	-СНО		95	12,667	6333
Me Br	-Et	Me Et	89	11,867	5933
-	-H	Me 2b	88	11,733	5866
	-Et	O <sub>2</sub> N-Et3a	85	11,333	5666
O <sub>2</sub> N-Br	-H	$O_2N$	92	12,267	6133
HO HO 4	-Et	HO $HO$ $HO$ $HO$ $HO$ $HO$ $HO$ $HO$	87	11,600	5800
	-Et	O H Br	95	12,667	6333

5a

#### TABLE 4 (Continued)

	(HO) <sub>2</sub> B- R <sub>2</sub> = CHO COM	$R_2 + R_1 + Br + Br + Catalyst 3 + K_2CO_3 + Fraction F$			
Aryl bromide	R <sub>2</sub>	Product	Yield <sup>b</sup> (%)	TON <sup>c</sup>	$TOF^{d}(h^{1-})$
	-H	o ⊢ → ↓ ↓ ↓ 5b	80	10,667	5333
MeOBr 6	-H	MeO	89	11,867	5933
	-CN	MeO-CN 6b	84	11,200	5600
Br 7	-Et	Ta	76	10,133	5066
Me Br	-Et	Me Et	96	12,800	6400
	-H	Me 8b	89	11,867	5933
	-CHO	H Contraction of the second se	93	12,400	6200
3		9a			

<sup>a</sup>Reaction conditions: 0.75 mmol aryl bromide, 1 mmol arylboronic acid, 1.5 mmol  $K_2CO_3$ , 12.5 ml DMF, 7.5  $\times$  10<sup>-3</sup> mol% of Pd-PH@GO-CSMNPs catalyst, 130°C, 2 h.

<sup>b</sup>Isolated yield.

 $^{c}$ TON = (turnover number, yield of product per mol of Pd).

 $^{\rm d}{\rm TOF} =$  (turn over frequency, TON/time of reaction).

Reactions with arylboronic acids contain the electron-withdrawing and electron-donating functional groups proceeded very well with a wide range of aryl bromides. Optimized conditions were determined to be the following: the use of Pd-PH@GO-CSMNPs as a catalyst, K<sub>2</sub>CO<sub>3</sub> as a base in DMF at 130°C. It is noteworthy that the activity of the catalytic reaction depends only on the surface exposed active sites and is regularly performed on the surface of the nano-magnetic catalyst. This promising trend could also improve and show better performance by supporting materials and adjusting the nanocrystallization of the particle size. From these studies, efficiency, easy recovery, and reusability show that the increased activity for the Pd-PH@GO-CSMNPs nano-magnetic catalyst compared with homogeneous analogs, exclusively originate from the carbon nanoparticle size, the presence of Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles (which in turn are a powerful catalyst) and palladium metal nanoparticles originate. These results predicted that the activation step of carbon halogen bonding in Pd-PH@GO-CSMNPs nano-magnetic catalyst and consequently catalytic activity increased significantly. After purification, all compounds were identified by <sup>1</sup>H NMR, <sup>13</sup>C NMR, and FT-IR spectroscopy (see Figures S3–S34 in the Supporting Information). In this study, outstanding TON and TOF (12,800/6400) were obtained using a very small amount of Pd-PH@GO-CSMNPs nano-magnetic catalyst and the findings are presented in Table 4. These results suggest that this catalyst can be used in most relevant industrial applications. To evaluate the catalytic performance of PH@GO-CSMNPs, its catalytic activity was compared with that of other palladium-based catalysts reported in the Suzuki-Miyaura reactions, and the results are presented in Table 5.

As can be seen from Table 5, PH@GO-CSMNPs catalysts show high reaction yields compared with other catalysts at lower reaction times. In addition, it is a superior ligand to some of the previously reported catalysts in terms of thermal stability, non-toxicity, and cheapness, ease of separation, reusability, and very low catalyst loading.

## 2.4 | Stability and recycling of the Pd-PH@GO-CSMNPs nano-magnetic catalyst

Finally, the recyclability of Pd-PH@GO-CSMNPs was investigated using the coupling of phenylboronic acid and 1-bromo-4-nitrobenzene in the presence of 0.0075 mol% of the catalyst under optimal conditions. As shown in Figure 14, this catalyst can be used up to five times without significant loss of catalytic performance.



**FIGURE 14** Catalytic recyclability test for successive five runs of 4-nitro-biphenyl. Reaction conditions: phenylboronic acid (1 mmol), 1-bromo-4-nitrobenzene (0.75 mmol), catalyst **3** ( $7.5 \times 10^{-3}$  mol %), DMF, 130°C and 2 h

**TABLE 5** Comparison results of PH@GO-CSMNPs catalyst with other palladium-based catalysts in the coupling reaction of aryl bromides and arylboronic acid

Entry	Pd Catalyst	Time (h)	Yield (%)	mol% of Pd	TON	TOF $(h^{1-})$	Ref.
1	GO-NHC-Pd	2	60	0.03	1079	540	[72]
2	GO-SB/Pd	5.6	85	0.8	106	19	[73]
3	Pd–G	20	74	0.1	740	37	[74]
4	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -4-AMTT-Pd(II)	3.5	60	0.1	600	171	[75]
5	Pd(II)–NHC	24	90	1.0	90	3.75	[76]
6	$\text{GO-NH}_2\text{-Pd}^{2+}$	4	80	1.0	80	20	[77]
7	GO-NHC-Pd <sup>2+</sup>	3	95	0.25	380	127	[19]
8	PdNPs	12	91	1.0	96	8	[78]
9	Pd-1/FSG	8	95	0.1	950	119	[79]
10	Pd(II)-MCM-4	24	54	$\times 10^{-3} 2.82$	329	13.7	[80]
11	PH@GO-CSMNPs	2	96	$\times 10^{-3}$ 7.5	12,800	6400	Present study

This magnetic catalyst retains 81% of its original catalytic activity at the end of the fifth cycle of Suzuki-Miyaura coupling reactions. These results indicate that Pd-PH@GO-CSMNPs is a highly stable catalyst that can be easily separated from the reaction mixture by a supermagnet for repeated use. To confirm the heterogeneity of the catalyst, we performed a hot filtration test for the coupling reaction between bromobenzene and phenylboronic acid using the Pd-PH@GO-CSMNPs catalyst under the same conditions according to previous studies.<sup>[81,82]</sup> The reaction was allowed to proceed under optimal reaction conditions for 1:20 h (yield of 75%), then the nano-magnetic catalyst was separated from the reaction mixture. After the reaction was continued for more than 30 min, no increase in the yield of the product was observed. This result confirms the heterogeneous nature of the nanocatalyst. However, the study of recycled Pd-PH@GO-CSMNPs composite shows another aspect of interest in this type of catalyst.As shown in Figure 15a,b, the TEM and FE-SEM images of the recovered catalyst after the fifth cycle show that the catalyst morphology remained unchanged. Moreover, the XRD and FT-IR spectra (Figure 15c.d) were studied in which they show no apparent changes in peaks for both fresh and recycled catalysts. These results show the good stability of the Pd-PH@GO-CSMNPs nano-magnetic catalyst.

## **3** | EXPERIMENTAL SECTION

#### 3.1 | Reagents and materials

MWCNT (average diameter 30 nm) has been purchased from Iranian Nanomaterials Pioneers

Co. (Mashhad, Iran). Natural graphite powder (>99.0%) obtained from Sigma-Aldrich. was The rest of the reagents and solvents used in research are commercially available and this purchased from commercial suppliers (Merck and Sigma-Aldrich).

#### 3.2 | Apparatus and measurements

FT-IR spectra were recorded using a Shimadzu 435-U-04 spectrophotometer through KBr plates in the wavelength range of 400–4000 cm<sup>-1</sup>. The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded with a 400-MHz Bruker or on a 90-MHz Jeol spectrometer using DMSO-d<sub>6</sub> or CDCl<sub>3</sub> as a solvent at room temperature. Also, melting points were measured using an SMPI apparatus. XRD pattern of the samples was recorded with an X' Pert Pro, Panalytical Co. at 25°C using monochromatic Cu K $\alpha$  radiation. The morphology of the samples was observed using an FE-SEM/EDS instrument (Zeiss, SMT AG, and TESCAN, MIRA3). Transmission electron microscopy (TEM) and TEM histogram were performed with a Phillips EM 2085 electron microscope. The Pd loading of nanocomposites was determined using inductively coupled plasma emission spectroscopy (ICP-OES) by (730-ES simultaneous CCD, Varian, USA). The magnetic behavior of nanoparticles was measured using a vibrating sample magnetometer (VSM) (MDKFT, Kashan, Iran). An ultrasonic water bath model parsonic 2600s (Pars Nahand Co., Iran) was applied for the homogeneous dispersion of samples.



**FIGURE 15** (a) TEM, (b) FE-SEM, (c) XRD, and (d) FT-IR analysis of PH@GO-CSMNPs catalyst after fifth recycling experiment

# 3.3 | Preparation of the nano-magnetic catalysts

## 3.3.1 | CNS-CSMNPs

To prepare nano-magnetic catalysts (**2** and **3**), silanization of the silica-coated magnetite nanoparticles on the CNSs was synthesized in three steps. The surface of the MWCNTs was oxidized in a manner previously reported in the literature.<sup>[83]</sup>

At first, 500 mg of MWCNT was added to 50 ml of  $H_2SO_4/HNO_3$  solution, and the suspension was refluxed for 4 h at 60°C. The oxidized MWCNTs were filtered and washed three times with 200 ml of deionized water and dried in a vacuum oven. Also, graphene oxide (GO) was first synthesized according to the method described by Hummers and Offeman from natural graphite powder.<sup>[84]</sup>

In the next step, FeCl<sub>3</sub>·6H<sub>2</sub>O (2.92g), and FeCl<sub>2</sub>·4H<sub>2</sub>O (1.07g) in 150 ml of deionized water under a nitrogen atmosphere were added to the oxidized CNSs (0.5 g) by vigorous stirring at 80°C. Then, 20 ml of 28% aqueous ammonia solution was added dropwise to the suspended solid nanoparticles under mechanical agitation. Next, the nanoparticles were separated by a supermagnet and washed three times with deionized water and methanol and then dried under vacuum (CNS-MNPs). In the following silanization of the silica-coated magnetite nanoparticles prepared according to the Stober and Moghanian method.<sup>[85,86]</sup> Dry particles (CNS-MNPs) (2 g) were dispersed in 100 ml dry ethanol and 30 min was sonicated. Then, 2.5 ml of 25 mol% concentrated aqueous ammonia solution and 7.5 ml (32.04 mmol) of tetraethylorthosilicate (TEOS) were added dropwise to the suspended solid nanoparticles under mechanical stirring and the reaction was refluxed for 20 h. After cooling the mixture, the resulting precipitate was separated from the solution using supermagnet; after several rinses with water, it was dried in a vacuum for 24 h (CNS-SMNPs). In the next step, 2 of the magnetic nanoparticles obtained in the previous step were dispersed in 100 ml of ethanol/ deionized water mixture (volume ratio, 10:1). Then, 3-chloropropyltrimethoxysilane (CPTMS) (2 ml) was added dropwise to the above suspension, and the above solution was stirred continuously for 18 h at 60°C. The resulting solid was collected by a supermagnet and washed three times with deionized water and ethanol and dried at 60°C (CNS-CSMNPs).

## 3.3.2 | PH@CNS-CSMNPs

The ligand, 5-(4-pyridyl)-5-phenylhydantoin (PH), was synthesized from 4-benzoyl-pyridine to ammonium

carbonate following a literature procedure by Eknoian–Webb reaction.<sup>[87]</sup> Hydantoin ligand solution (0.5 g) in 100 ml of ethanol, a few drops of trimethylamine and 0.5 g (CNS-CSMNPs) were added to a flask under ultrasound irradiation for 30 min at 50°C. Then the reaction under reflux conditions was stirred for 4 h in a nitrogen atmosphere. The reaction mixture was then cooled to room temperature, and the nanoparticles were collected by magnets and washed three times with ethanol.

## 3.3.3 | Pd-PH@CNS-CSMNPs

The palladium (II) chloride was immobilized on the surface of PH@CNS-CSMNPs by reacting PH@CNS-CSMNPs with PdCl<sub>2</sub> in 50-ml ethanol. For this purpose, 0.75 g (5.5 mmol) of PdCl<sub>2</sub> was added to 1 g of well-dispersed PH@CNS-C

SMNPs in 40-ml of ethanol. The mixture was stirred for 24 h at 60°C. The obtained product, which is Pd(II) complex anchored on the surface of functionalized magnetic carbon nanostructures (designated as Pd-PH@CNS-CSMNPs), was washed with 60 ml of acetoneethanol mixture (1:1, v/v) (three times each time with 20 ml) to remove the excess PdCl<sub>2</sub>, and prepared suspension was collected by supermagnet then dried in an oven at 60°C for 24 h. In the next step, a nano-magnetic catalyst (1) was synthesized.  $Fe_3O_4$  NPs were also prepared using the chemical co-precipitation technique. An aqueous solution of salts FeCl<sub>3</sub>.6H<sub>2</sub>O (2.92 g) and FeCl<sub>2</sub>.4H<sub>2</sub>O (1.07 g) in deionized water at 80°C with the addition of NH<sub>4</sub>OH (25%, 15 ml) was mixed under rapid stirring and the product was a black powder. The black precipitate was magnetically separated and washed with ethanol and water (volume ratio, 2:1) and dried at 60°C. The rest of the steps were performed according to the method mentioned above.

# 3.4 | General experimental procedure for Suzuki cross-coupling reaction

Based on optimized conditions, a 10-ml oven-dried containing a magnetic stirring bar was charged with a nanomagnetic catalyst ( $7.5 \times 10^{-3}$  mol%), aryl bromide (0.75 mmol), arylboronic acid (1 mmol), K<sub>2</sub>CO<sub>3</sub> (1.5 mmol), and DMF (12.5 ml) were added, and the reaction was sealed and stirred at 130°C for a specified time. The reaction mixture was then cooled to room temperature. After solvent evaporation, the crude product was purified by thin-layer chromatography (TLC) and analyzed by FT-IR, <sup>1</sup>H, and <sup>13</sup>C NMR (see Supporting Information). Yields were calculated against the consumption of the aryl bromides.

## 4 | CONCLUSIONS

Here, we have prepared highly dispersible, recyclable, and reusable catalysts based on iron and carbon nanostructures (graphene oxide/multi-walled carbon nanotubes) with a simple process and analyzed by various analytical methods. These catalysts were magnetically active, so due to their magnetic iron oxide nanoparticles, carbon nanostructure, and palladium metal, they were a great potential application for catalysis in the Suzuki-Miyaura coupling reactions. The response surface methodology with Box-Behnken design was used to determine a feasible experimental design to optimize the coupling conditions of the Suzuki–Miyaura reactions. A comparative studv between Fe<sub>3</sub>O<sub>4</sub> NPs, CNT, and GO-supported nanocatalyst indicates that the GO-supported catalyst has a superior catalytic activity compared to other catalysts. The three parameters of solvent ratio, catalyst loading, and reaction time have the most significant effect on production. The experimental results indicated that the optimum conditions for the nano-magnetic catalyst Pd-PH@GO-CSMNPs were 12.5 ml of dimethylformamide,  $7.5 \times 10^{-3}$  mol% catalyst, and 2 h reaction time. The effect of all three independent parameters was statistically investigated on the yield for biphenyl production at 130°C. The temperature was the most critical factor in this reaction. Most importantly, the catalyst is quite easy to recycle and has excellent recvclability even after five cycles without losing efficiency. The heterogeneous catalysts produced on these bases are the basis for future nanocomposites with their inherent recovering and multi-functionalizable properties.

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#### AUTHOR CONTRIBUTIONS

**Faezeh Moniriyan:** Data curation; formal analysis; investigation; methodology; project administration; software. **Seyed Javad Sabounchei:** Conceptualization.

#### DATA AVAILABILITY STATEMENT

The data that supports the findings of this study are available in the supporting information of this article.

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