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Green Synthesis of Pd NPs/ Crataegus Kernel Catalyst using *Lotus corniculatus L.* Extract for the Reduction of 4-nitrophenol and Hexavalent Chromium

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Abstract

Nitrophenol compounds and hexavalent Chromium are two of the most harmful pollutants in wastewaters widely used in various industries. Therefore, removal of these harmful pollutants is essential. In this research, the extract of the plant of *Lotus corniculatus L.* was used for green synthesis of Pd nanoparticles (NPs) supported on Crataegus kernel as an environmentally benign support. Pd NPs/ Crataegus kernel as an effective catalyst was prepared through the reduction of Pd^{+2} ions using *Lotus corniculatus L.* extract as the reducing and capping agent and Pd NPs immobilization on Crataegus kernel surface in the absence of any stabilizer or surfactant. According to FT-IR analysis, the hydroxyl groups of phenolic in *Lotus corniculatus L.* extract as bioreductant agents are directly responsible for the reduction of Pd^{+2} ions and the formation of Pd NPs. The as-prepared catalyst was characterized by Fourier transform infrared (FT-IR) and UV-Vis spectroscopy, field emission scanning electron microscopy (FE-SEM) equipped with an energy dispersive X-ray spectroscopy (EDS), and X-ray diffraction analysis (XRD). The synthesized catalyst was used in the reduction of chromium (VI) and 4-nitrophenol (4-NP) at room temperature. The Pd NPs/ Crataegus kernel showed excellent catalytic activity in the reduction of these compounds. In addition, it was found that Pd NPs/ Crataegus kernel can be recovered and reused several times without significant loss of catalytic activity.

Keywords: Pd NPs, Crataegus kernel, Green synthesis, *Lotus corniculatus L.* extract, Chromium (VI), 4-NP.

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Introduction

Over the past few years, toxic pollutants that are widely used in various industries and improper management of wastewater treatment, have caused a serious threat to human health. Hexavalent chromium (Cr (VI)) and and 4-nitrophenol (4-NP) are widely used in various industries, the release of these toxic, bio-refractory, chemically stable and carcinogenic pollutants into the waste water has become one of the major sources of water pollution in the environment [1-3].

Adsorption and chemical coagulation, which are two common techniques for wastewater treatment, cannot be sufficient and effective in the degradation of these compounds to non-dangerous products because of their high resistance, high stability and, low solubility in water. Therefore, it is necessary to find effective methods to remove these contaminants [1-7].

Recently, researchers concluded that chemical reduction in the presence of metal nanoparticles is one of the most effective methods for removing toxic, bio-refractory, chemically stable, and carcinogenic pollutants such as Cr (VI) and 4-NP [8, 9].

Among various MNPs, Pd NPs have been paid much attention to during the past decade due to their unique electrical, optical, and biological properties. Furthermore, having a high surface-to- volume ratio, Pd nanoparticles (Pd NPs) can dramatically enhance the interaction between reactants and catalysts. Additionally; heterogeneous nanocatalysts can easily separate products from the reaction mixture to form recyclable catalysts [8-10].

Bio-derived materials are alternative environmentally benign supports in this regard. The advantages of biological methods compared with other methods are: no costly and poisonous capping agents or stabilizers are required, high-temperature calcination are not necessary for the preparation of the final product, no poisonous organic solvent or hazardous materials are required and the methods can be easily scaled up. A metal NP preparation method using various plant extracts or tree gums has recently been reported. However, the agglomeration of metal NPs during catalytic reactions is unavoidable [11].

Newly, our research group reported the green synthesis of MNPs supported on the various inorganic supports such as clinoptilolite, TiO_2/SiO_2, and agricultural biowaste involve some of the fruit kernel shells and overcome the drawbacks concerning stability and recovery of MNPs [7-16]. According to the literature and our previous works, Crataegus kernel powder as a biowaste material seems to be suitable support for adsorption purposes due to its high surface area. Crataegus kernel is a composite material mainly comprised of cellulose, hemicellulose, lignin, and minor amounts of other organic compounds. The main elements present in the Crataegus kernel are carbon, hydrogen, oxygen, and nitrogen.

Several of physical and chemical methods for the synthesis of nanoparticles are available. These methods require high temperature and pressure conditions and mainly use toxic and hazardous reactants and starting materials. Thus, the development of a simple method for the synthesis of well-dispersed, stable MNPs and their immobilization on an effective support is highly desirable. Plant extracts have been used as reducing and capping agents in the green synthesis of MNPs with high yields. These synthetic methods are cost-effective, environmentally friendly, and organic solvent-free, easy to work up, and suitably scaled up. In fact, when a nanostructure is synthesized using a plant, the phytochemicals adsorbed on the nanosurface and besides many other benefits such as green synthesis, increase the stability, preventing the agglomeration and deforming of nanoparticles in most cases, they as capping agents cause better adsorption of reactants on nanosurface and therefore, enhance the yield of the reactions [7-18].

To date, there is no report on the biosynthesis of the Pd NPs by using extract of *Lotus corniculatus L.* extract. *Lotus corniculatus L.* is known as a bird’s foot trefoil and belongs to the *Leguminosae* family. It can fix nitrogen utterly root nodules making it beneficial as a cover crop. Hence, in our experiment, *Lotus corniculatus L.* extract has been used to synthesize [19].

In the present work, we describe the synthesis of Pd NPs/Crataegus kernel using *Lotus corniculatus L.* extract via reduction of the Pd^{2+} ions by using *Lotus corniculatus L.* extract as a reducing and stabilizing agent. The synthetic catalyst was utilized in the reduction of 4-NP and Cr (VI) in water at room temperature.

Experimental

Instruments and reagents

Reagents were all obtained from Merck and Aldrich Chemical Companies and used without further purification. A Varian model 640 spectrophotometer was used to record IR (KBr) spectra. A Philips model X'PertPro diffract meter X-ray diffraction equipped with a graphite monochromatic crystal was used to perform X-ray diffraction (XRD) measurements. The X-ray wavelength was 1.5405 A° and the diffraction patterns were recorded in the 2θ range (10–80) with a scanning speed of 2°/min. Scanning electron microscopy (SEM) (Cam scan MV2300) was used to investigate the morphology and particle dispersion. EDS (Energy Dispersive X-ray Spectroscopy) performed in SEM was used to measure the chemical composition of the prepared nanostructures. The chemical analysis of prepared nanostructures was carried out by EDS (S3700N). A double beam Perkin Elmer Lambda 25 UV–Vis spectrophotometer was used to record UV–Visible spectral analysis.

Preparation of Lotus corniculatus L. extract

The leaves of the *Lotus corniculatus L.* was provided from Qom center of medical plants and then dried leaves of the *Lotus corniculatus L.* (10 g) were powdered and refluxed at 75 °C with ethanol solution 70% (V/V) (100 mL) for 30 min. The mixture was then cooled to ambient temperature, and the aqueous extract was centrifuged at 6000 rpm, followed by filtration through no. 1 Whatman filter paper to obtain an aqueous extract. The extract thus filtered was stored at 4 °C for further use [3,7].

Green synthesis of the Pd NPs using Lotus corniculatus L. extract

Lotus corniculatus L. extract was used as a reducing and stabilizing agent. To prepare Pd NPs, 20 mL of 5 mM Pd $(NO_3)_2$ solution was added dropwise to plant extract (50 mL) in a 100-mL conical flask and the resulting mixture was refluxed at 80 °C for 2 h. The reaction mixture color gradually changed in 10 min, indicating the formation of Pd NPs. Next, the colored solution was centrifuged at 6000 rpm for 30 min for complete precipitation of Pd NPs. The precipitate thus obtained was washed three times using ethanol and air dried for 24 h at 50°C in an oven [3, 7].

Preparation of the Pd NPs/ Crataegus kernel

The Crataegus kernel was provided in August 2016 from Qom center of medicinal plants First, prior to use, the Crataegus kernel was washed and dried at 90 °C for 6 h in an oven, and mechanically pretreated by crushing in a mill, followed by sieving to separate <40-µm particle size fractions. Following the pretreatment of Crataegus kernel, the dried powdered the Crataegus kernel (1.0 g) was mixed with aqueous plant extract (40 mL) in a 100-mL conical flask and then 20 mL of a 0.03 M aqueous solution of the Pd $(NO_3)_2$ was added dropwise. The mixture obtained was then heated at 80 °C while vigorously shaking for 2 h until the mixture color gradually changed, indicating the formation of Pd/Crataegus kernel nanocomposite, as monitored by UV-Vis. The product was then filtered [20].

Reduction of 4-NP and Cr (VI) by Pd NPs/ Crataegus kernel

In a typical reduction experiment, 4-nitrophenol aqueous solution (2.5 mM, 25 mL) was mixed with Pd/ Crataegus kernel (3.0 mg) and stirred constantly for 2 min. Freshly prepared aqueous $NaBH_4$ solution (0.25 M, 25 mL) was then added to the resulting mixture at room temperature, and it was allowed to stir at ambient temperature until the deep yellow solution became colorless, which indicates the completion of 4-NP degradation. Moreover, catalytic degradation of 25 mL of 3.4 mM aqueous solution of Cr (VI) was carried out by adding 1.0 mL formic acid solution (88%) at room temperature while stirring. After 2 min, 3.0 mg of Pd NPs/Crataegus kernel powder was added at room temperature, and the stirring continued. The Cr (VI) concentration was then determined using an indirect UV–visible spectrophotometric method based on the reaction of Cr (VI) and diphenylcarbazide, which forms a red–violet colored complex. Finally, the absorbance of the colored complex was measured in a double-beam spectrophotometer at 540 nm wavelength [3].

Results and discussion

Characterization of Lotus corniculatus L. extract and Pd NPs

The UV-Vis analysis of *Lotus corniculatus L.* extract and Pd NPs was performed and results are shown in Figure 1.

The UV spectrum of *Lotus corniculatus L.* extract (Fig. 1(a)) shows bands at around 282 and 338 nm, assigned to the $\pi \rightarrow \pi^*$ transitions which can be attributed to the presence of polyphenolics. The presence of flavonoids and phenolic acids in the extract could be responsible for the reduction of Pd^{2+} ions and the formation of the corresponding Pd NPs In fact, phenolic compounds especially flavonoids to which are attributed many of the antioxidant properties, due to supporting a green reducing media through their hydrogen donation ability and structural requirements considered to be essential for effective radical scavenging and production of nanoparticles. Moreover, flavonoids and phenolic acids within the extract were oxidized during the reduction of Pd^{2+} ions to Pd^0 [13].

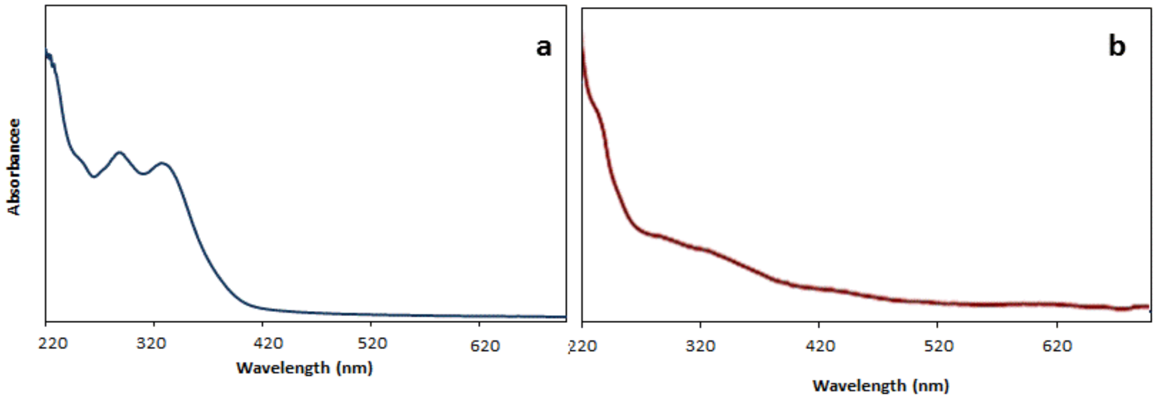


Figure 1. UV-Vis spectra of *Lotus corniculatus L.* extract (a) and green synthesized Pd NPs using *Lotus corniculatus L.* extract (b).

The reduction of the Pd ions by *Lotus corniculatus L.* extract and the formation of Pd NPs was monitored by UV-Vis spectroscopy, as well (Fig. 1(b)). After the addition of Pd^{2+} solution to *Lotus corniculatus L.* extract, the color of the solution changes into dark brown, indicating the formation of Pd^o from Pd^{2+} ions. The progression of the reaction and formation of the Pd NPs were controlled by UV-Vis spectroscopy. In addition, the investigation of the stability of synthetic NPs using UV-Vis spectrophotometry shows that biosynthesized NPs by this plant are completely stable with no appreciable variations in the shape, position, and symmetry of the absorption peak even after 2 weeks [13].

To illustrate the possible functional groups of *Lotus corniculatus L.* extract for the reduction of Pd^{2+} to synthesized Pd NPs, the FT-IR analysis was performed and results are shown in Fig. 2. As observed in Fig. 2 (a) *Lotus corniculatus L.* extract showed some peaks at 3392, 2922 and 1068-1270 cm^{-1}, which are related to free hydroxyl groups, C-H and C-OH stretching vibrations, respectively. Moreover, the absorption band at about 1624 cm^{-1} is due to carbonyl group vibration and the band at 1428 cm^{-1} can be assigned to the stretching C=C aromatic rings [19]. These peaks suggest the presence of flavonoids and phenolic acids in the *Lotus corniculatus L.* extract. The presence of flavonoids and phenolic acids in the extract could be responsible for the reduction of Pd^{2+} ions and the formation of the corresponding Pd NPs [21, 22]. Flavonoids and phenolic acids within the extract were oxidized during the reduction of Pd^{2+} ions to Pd^{o}. According to the results obtained from the FT-IR study of synthesized Pd NPs by using *Lotus corniculatus L.* extract (Fig. 2(b)), the positions of observed peaks are almost similar to the corresponding peaks in the FT-IR spectrum of *Lotus corniculatus L.* extract, which shows that the organic compounds in the extract are absorbed on the surface of Pd NPs by π-electron interaction [7, 13]. These results show that the polyphenolics could be adsorbed on the surface of Pd NPs, possibly by interaction through π–electron interaction in the absence of other strong legating agents.

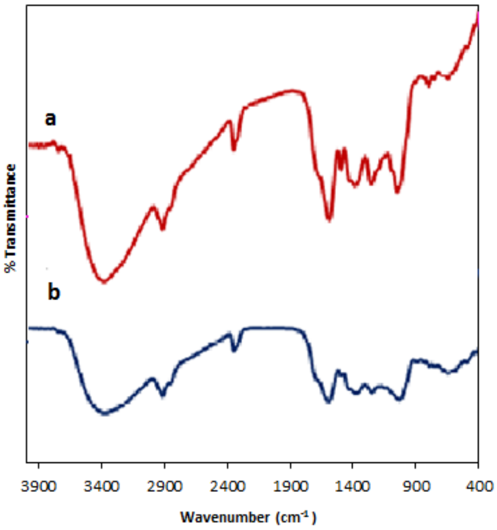


Figure 2. FT-IR spectra of *Lotus corniculatus L.* extract (a) and green synthesized Pd NPs using *Lotus corniculatus L.* extract (b).

Characterization of Crataegus kernel and Pd NPs/ Crataegus kernel

As is clear, cellulose, hemicellulose, and lignin three are main components of biomass in the Crataegus kernel. Therefore, the typical functional groups for these compounds are expected in FT-

IR spectra. The broad peak observed around 3100–3500 cm^{-1} in the spectra of the Crataegus kernel and Pd NPs/ Crataegus kernel corresponds to free OH in molecule and OH group forming hydrogen bonds of stretching groups of macromolecular association. The absorption band at 2920 cm^{-1} is related to the C-H stretching vibrations. Another small absorption peak at 1612 cm^{-1} can be associated with the bending vibrations of H_2O molecules. In addition, the absorption bands at 1365 and 1460 cm^{-1} indicate the presence of the chemical functional groups, – CH_3, –CH_2, and –CH, which are characteristic of alkanes, cellulose, hemicellulose, and lignin. In addition, the absorbance at 1732 cm^{-1} is due to the C=O stretching vibrations. Moreover, the peaks at 1250 and 1057 cm^{-1} can be attributed to the C–O–C and C–O–(H) functional groups [13]. No changes occur in functional groups after the immobilization of Pd NPs on the Crataegus kernel, as verified by the FT-IR studies of the Crataegus kernel and Pd/ Crataegus kernel nanocomposites.

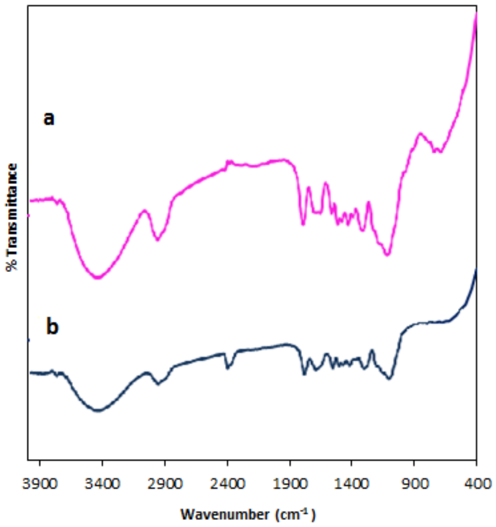


Figure 3. FT-IR spectra of Crataegus kernel (a) and Pd NPs/ Crataegus kernel (b).

To investigate the phases of the samples, XRD measurements were performed. The broad peak in the XRD of the Crataegus kernel sample (Fig. 4) at 2θ value of 22.0° reveals the presence of an amorphous phase of the Crataegus kernel. The peak, which is only one due to the Crataegus kernel, mainly consists of cellulose, hemicelluloses, and lignin [13]. Pd/ Crataegus kernel nanocomposite XRD pattern shows many new diffraction peaks compared to Crataegus kernel. The diffraction peaks appear at 2θ values of 20.0°, 28.8°, 40.0°, 47.8°, 50.1°, and 67.1° which well match with the JCPDS card of Pd (No: 87-0641). XRD results confirm the purity of the synthesized Pd NPs, without any impurities such as PdO [7, 13, 23, 24].

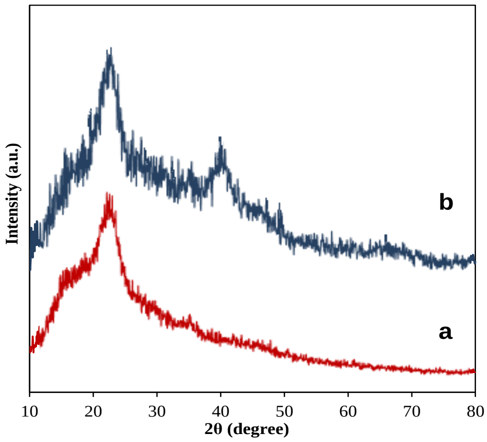


Figure 4. XRD pattern of Crataegus kernel (a) and Pd NPs/ Crataegus kernel (b).

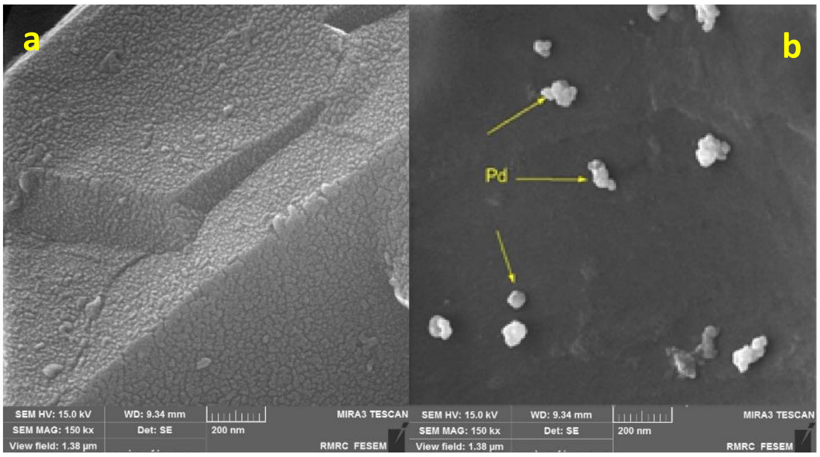


Figure 5. FE-SEM image of Crataegus kernel (a) and Pd NPs/ Crataegus kernel (b).

Typical FE-SEM images of the as-produced Crataegus kernel and Pd NPs/ Crataegus kernel nanocomposite are shown in Fig. 5. The particles of Crataegus kernel powder consist of a highly porous structure according to the literature and Fig. 5; Fig. 5 (b) clearly shows that the presence of Pd NPs has caused changes in the roughness of the surface. The Pd particles are of spherical morphology and have very narrow diameters with average sizes of about <20 nm and are uniformly distributed on the Crataegus kernel surface.

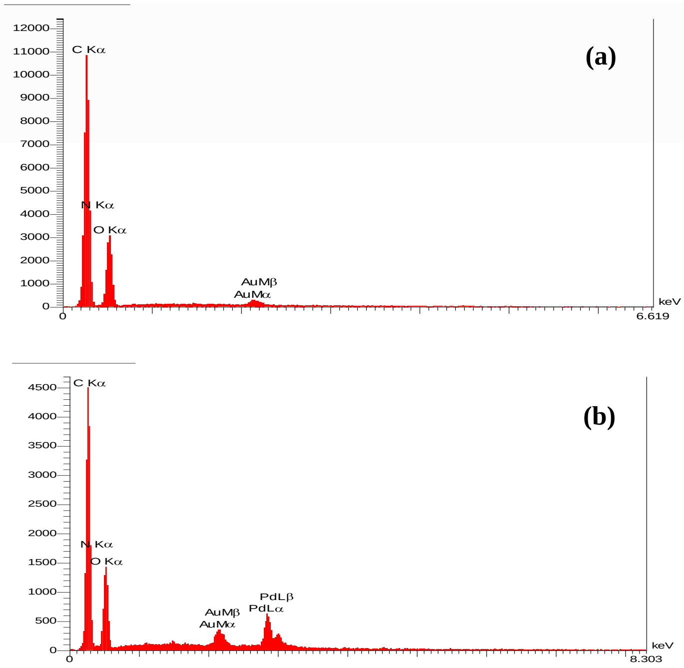


Figure 6. EDS spectra of the Crataegus kernel (a) and Pd NPs/ Crataegus kernel (b).

The elemental composition of the Crataegus kernel and Pd NPs/ Crataegus kernel sample was also studied by the EDS spectrum and the results are shown in Fig. 6. EDS results confirm that C, O, and N elements exist in the Crataegus kernel (Fig. 6(a)). Moreover, the EDS spectrum of the Pd NPs/ Crataegus kernel indicates that this sample is composed of Pd, C, O, and N (Fig 6 (b)).

Evaluation of the catalytic activity of the Pd NPS/ Crataegus kernel

Catalytic reduction of 4-NP

In this research, the catalytic performance of the Pd NPs/Crataegus kernel in the reduction of 4-NP to 4-AP in the presence of $NaBH_4$ in water was evaluated. In the absence of the Pd NPs/Crataegus kernel, the reduction process was not complete in 150 min. Firstly, the reduction of 25 mL of 4-NP aqueous solution (2.5 mM) using 10 mg of Crataegus kernel powder in the presence of 25 mL of $NaBH_4$ (0.25 M) was examined at room temperature, but after 150 min, no changes were observed. In another reduction experiments, the effects of $NaBH_4$ and catalyst concentrations and different amounts of catalyst and $NaBH_4$ on the catalytic reduction of 4-NP to 4-AP were studied and the results are shown in Table 1. According to the UV-Vis spectrum, the aqueous solution of 4-NP exhibits an intense absorption about at 315 nm. After the addition of $NaBH_4$, a redshift of the peak of 4-NP from 315 to 400 nm was observed, and the color of the solution altered from light. After the addition of the Pd NPs/Crataegus kernel into the reaction system, the reduction process was monitored by UV-Vis spectroscopy of the reaction solution. As observed in the UV-Vis spectrum, the absorption peak at 400 nm fully disappeared in the presence of the catalyst and a new peak at about 297 nm appears which is ascribed to the 4-AP product with increasing the reaction time.

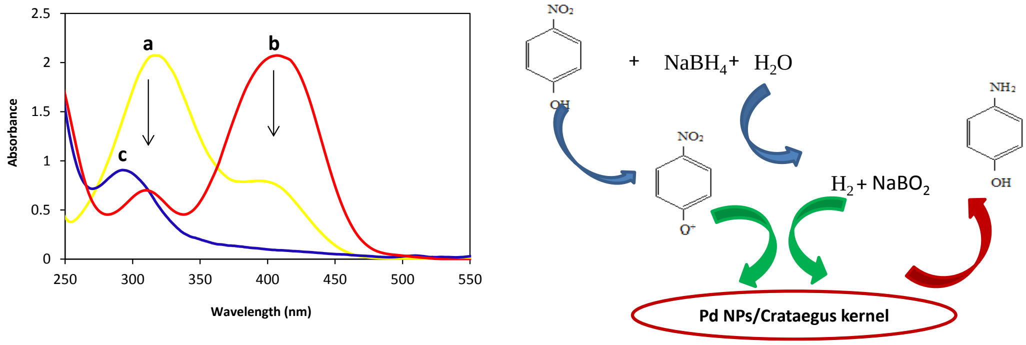


Figure 7. UV-Vis absorption spectra of 4-NP (a); 4-NP + $NaBH_4$ (b) and 4-AP (c) and The proposed mechanism for the reduction of 4-NP to 4-AP in the presence of Pd NPs/Crataegus kernel and $NaBH_4$.

In addition, the yellow color of the 4-nitrophenol solution vanishes and ultimately becomes colorless (4-AP) [13, 21, 22]. The reduction process was monitored by using UV-Vis measurements at room temperature, and the results are shown in Fig. 7.

According to Table 1, the catalytic efficacy increased with an increase in the amount of $NaBH_4$ and catalyst. This means lower reduction times were observed for higher $NaBH_4$ and Pd NPs/Crataegus kernel amounts. The best result was obtained with 250 mM (100 equivalents) of $NaBH_4$ and 7.0 mg of catalyst.

Table 1. Completion time for the reduction of 4-NP (2.5 mM) to 4-AP using different amounts of Pd NPs/Crataegus kernel and $NaBH_4$.

Entry	Catalyst (mg)	[$NaBH_4$] (mM)	Time (s)
1	3	125	184
2	3	187.5	132
3	3	250	43
4	5	125	52
5	5	187.5	38
6	5	250	29
7	7	125	39
8	7	187.5	34
9	7	250	19

Catalytic reduction of Cr (VI)

The Pd NPs/Crataegus kernel was also used to reduce Cr (VI) in the presence of formic acid. The progress of the reduction reaction was monitored using an indirect UV–visible spectrophotometric method based on the reaction of the remained of Cr (VI) and diphenylcarbazide, which forms a red–violet colored complex (Scheme 1). Finally, the absorbance of the colored complex was measured in a double-beam spectrophotometer at 540 nm wavelength (Fig. 8) [3].

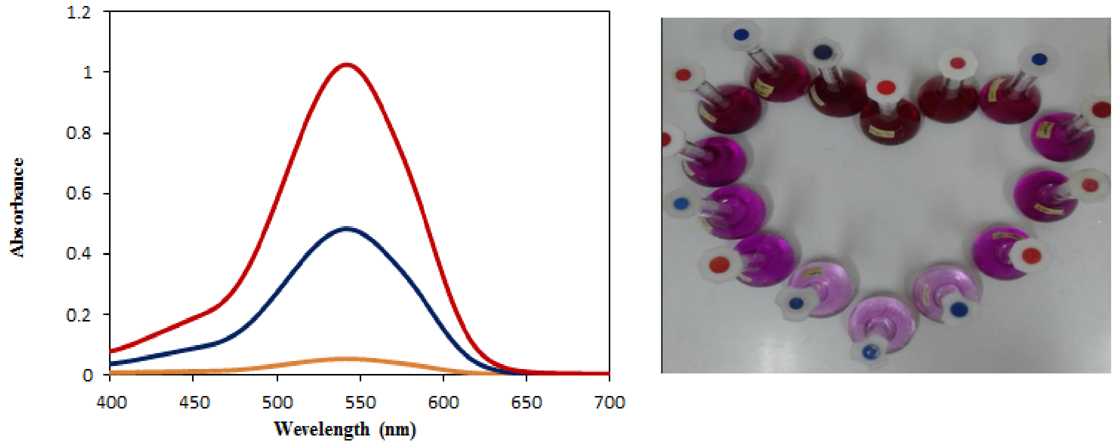
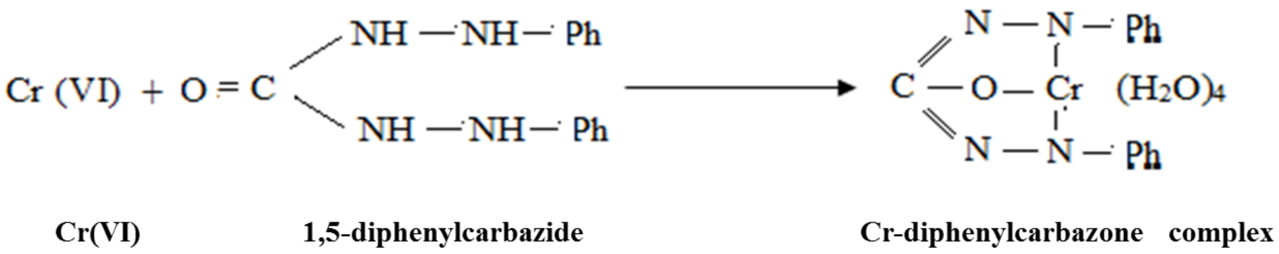
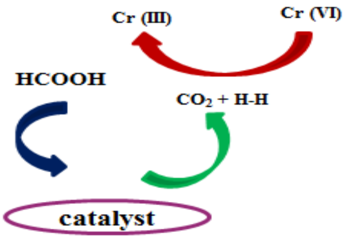


Figure 8. The UV-Vis spectra of Cr - diphenylcarbazone complex.

It is well known that formic acid with potent reducing features in the presence of the nanocatalyst can be easily decomposed to CO_2 and H_2 without the production of intermediate materials. Reduction of Cr (VI) to Cr (III) is accomplished through hydrogen transfer (Scheme 2). As can be seen in Fig. 8, during 4 min, the reduction of Cr (VI) to Cr (III) is progressing about 98 percent. Optimum conditions included 5.0 mg Pd NPs/Crataegus kernel, and 2.0 mL of formic acid [3, 25].



Scheme 1. Structure of 1, 5- diphenylcarbazide and Cr - diphenylcarbazone complex.



Scheme 2. The proposed mechanism for the reduction of Cr (VI) to Cr (III) in the presence of Pd NPs/Crataegus kernel and Formic acid.

Evaluation of the recyclability of the catalyst

It is well known that, the level of recyclability is one of the most important factors affecting the practical application of the heterogeneous catalyst, especially for commercial and industrial applications. The recyclability of synthesized catalysts in this work in the reduction of 4-NP with $NaBH_4$ was investigated. At the end of the reaction, the catalyst was separated from the reaction mixture by brief centrifugation and multiple washings with distilled water followed by drying and reused in the next cycle. The catalyst was reused at least seven times for 100% reduction of 4-nitrophenol and without significant loss of catalytic activity, as monitored by UV-Vis spectroscopy. A little decrease in efficiency was observed after the 8th cycle. These results demonstrate the high stability and catalytic activity of the catalyst under the operating conditions. In addition, the catalytic efficiency of the catalyst remained almost constant up to six cycles of operation and the time required for 100% reduction of Cr (VI) was found to be approximately the same up to the 7th cycle.

Conclusion

In this article, a rapid, convenient, biocompatible, and efficient method is developed for the synthesized Pd NPs/Crataegus kernel using *Lotus corniculatus L.* extract as a reducing and stabilizing agent. Pd NPs/Crataegus kernel was utilized in the reduction of 4-NP and Cr (VI) in water at room temperature. SEM, XRD, EDS, FT-IR, and UV-Vis spectroscopic techniques were used to characterize the synthetic Pd NPs/Crataegus kernel. Also, results revealed that Pd NPs/Crataegus kernel had the highest catalytic activity in comparison with the other literature. Moreover, recycling results confirm that the catalyst can be recycled several times for 100%.

According to these advantages, the Pd NPs/Crataegus kernel can be regarded as a promising catalyst in the reduction of organic dyes.

List of abbreviations

Fourier transform infrared	FT-IR
UV-Vis spectroscopy	UV-Vis
Equipped with an energy dispersive X-ray spectroscopy	EDS
X-ray diffraction analysis	XRD
Field emission scanning electron microscopy	FE-SEM
4-nitrophenol	4-NP
hexavalent Chromium	Cr(VI)
Palladium non particles	Pd NPs

Acknowledgments

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