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# Magnetic Fe<sub>3</sub>O<sub>4</sub>/Graphene Oxide/Copper-Based Nanocomposite as a Reusable Catalyst for the Reduction of 4-Nitrophenol

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In the present investigation,  $Fe_3O_4/Graphene oxide/Pr-NH_2-Cu^{II}$  was reported as a novel magnetically recoverable nanocomposite and characterized using various analytical techniques such as FT-IR spectroscopy, field emission scanning electron microscopy (FE-SEM), energy dispersive X-ray spectroscopy (EDX), vibrating sample magnetometry (VSM), X-ray diffraction (XRD), and inductively coupled plasma (ICP). The catalytic performance of the synthesized catalyst was evaluated in the reduction of 4-nitrophenol to 4-aminophenol by an excess amount of sodium borohydride as the source of hydrogen in aqueous solution. The reaction was monitored by UV-vis spectroscopy at ambient temperature. Magnetic nature of the catalyst led to its simple recovery by a permanent magnet and excellent recyclability without appreciable loss of the catalytic activity.

**Keywords:** 4-Nitrophenol Reduction, Fe<sub>3</sub>O<sub>4</sub>-MNPs, Graphene Oxide, NaBH<sub>4</sub>, Copper (II) Supported Catalysts. Delivered by Ingenta

# **1. INTRODUCTION**

Nitrobenzene and its derivatives are widely used as important organic feedstocks in the chemical industry for the production of dyes, pigments, pharmaceuticals, plastics, fungicides, pesticides, industrial solvents, and explosives [1, 2]. However, these compounds are highly hazardous to the environment and human health [3]. As a member of nitroaromatic compounds, 4-nitrophenol is one of the most refractory organic pollutants which extensively exists in industrial effluents of chemical plants and agricultural waste-waters [4]. This compound is toxic and due to its minuscule biodegradability, high stability and solubility in water is stable in the environment and biological systems which can cause serious damage to the central nervous system, liver, and kidney of humans and animals even at low concentration [5-7]. For this reason, the United States Environmental Protection Agency (EPA) has classified 4-nitrophenol as 'priority pollutant.' Therefore, it is of great importance to assess the fate of this compound in the environment and develop convenient procedures to remove it from waste-water before

discharge. Many methodologies have been reported for the removal of 4-nitrophenol from contaminated water such as photocatalytic degradation [8], catalytic reduction [9], microwave-assisted catalytic oxidation [10], electrochemical treatment [11], biodegradation [12], electro-Fenton method [13], and so on. Among the above-mentioned procedures, the catalytic reduction of 4-nitrophenol to 4-aminophenol in aqueous solution has been proved to be an efficacious, cost-effective and clean method for this purpose [14]. 4-aminophenol is a vital intermediate for the synthesis of many analgesic and antipyretic drugs. Also, it is used extensively as a corrosion inhibitor, photographic developer, hair-dyeing agent, anticorrosion-lubricant [15]. Hence, it is very important to design an efficient and environmentally benign catalytic system for the reduction of 4-nitrophenol to 4-aminophenol.

In recent years, magnetic nanoparticles (MNPs) have attracted more attention because of their widespread range of applications in environmental remediation, drug delivery, magnetic resonance imaging (MRI), energy storage, magnetic inks, magnetic fluids, and catalysis [16, 17]. In the field of organic chemistry, the use of MNPs as catalysts or catalyst supports (magnetic nanoparticles

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supported catalytic systems) in organic transformations has become a hot topic of numerous investigations. This is because MNPs can be easily (via external magnet) separated and recovered which is very worthwhile from the viewpoint of economic and environmental issues (green chemistry) [18, 19].

Among the various types of MNPs, more attention has been paid to the  $Fe_3O_4$  nanoparticles because of their unique properties such as simple synthesis, inexpensiveness, low toxicity, biocompatibility, good super paramagnetic property and having a very active surface for adsorptions and immobilization of ligands, metals and catalytic species [20–22]. On the other hand, due to their higher surface energy,  $Fe_3O_4$  nanoparticles may rapidly aggregate and convert to bulkier form. So, to overcome this drawback, improving the chemical stability and also to achieve some advantages as the versatility in surface modification, this compound is generally coated with various organic or inorganic materials and recently graphene oxide [23].

Graphene oxide, an attractive class of carbon-based nanomaterial, is an excellent eco-friendly candidate for protection of Fe<sub>3</sub>O<sub>4</sub> MNPs because of its exceptional properties such as mechanical stability, large surface area, tunable electrical and optical properties [24]. Moreover, the abundant of several types of oxygen-containing functional groups including epoxy, hydroxyl groups and carboxylic acids on the large surface area of Graphene oxide not only leads to excellent aqueous dispersity but also provide efficacious anchoring sites to immobilize desired species and further chemical modifications [25–27]. On the other hand, copper-based catalysts play an important role in chemical transformations. In the last decade, a number of copper-based catalytic systems have been used for the conversion of the nitro group to amine [28–34]. Due to the remarkable results of these studies and on the basis of the above considerations, we were interested to investigate the applicability of Fe<sub>3</sub>O<sub>4</sub>/Graphene oxide/Pr-NH<sub>2</sub>-Cu<sup>II</sup> as a novel magnetically recoverable catalyst for the reduction of 4-nitrophenol to 4-aminophenol in the presence of sodium borohydride.

# 2. EXPERIMENTAL DETAILS

#### 2.1. Materials and Methods

Highly pure Chemicals were purchased from Sigma-Aldrich, Fluka and Merck Chemical Companies and used without further purification. X-ray diffraction (XRD) measurements were performed using Panalytical X'Pert Pro instrument. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker Alfa FT-IR spectrometer using pressed KBr pellets at room temperature. Morphology and particle size were studied by field emission scanning electron microscope (FE-SEM) (MIRA3 TESCAN). The chemical composition of the catalyst was determined using energy dispersive X-ray analyzer (EDX). Elemental analysis of Cu was carried out using inductively coupled plasma-optical emission spectrometry (ICP-OES) (Optima 7300D-PerkinElmer). Magnetization curves were recorded by a vibrating sample magnetometer (VSM, Meghnatis Daghigh Kavir) at room temperature. UV-visible spectra were acquired with a T60UV UV-VIS spectrophotometer.

# 2.2. Preparation of Fe<sub>3</sub>O<sub>4</sub>/Graphene Oxide Nanocomposite

Graphene oxide was prepared from graphite according to the modified Hummers method [35, 36]. To synthesis of the  $Fe_3O_4/Graphene$  oxide nanocomposite (with  $Fe_3O_4$  to Graphene oxide mass ratio of 10) [37], Graphene oxide (0.25 g) was dispersed in distilled water (30 mL). Then ethanol (40 mL) was added and the mixture was sonicated for 20 min. FeCl<sub>3</sub> · 6H<sub>2</sub>O (5.84 g 3.52 mmol) and FeCl<sub>2</sub> · 4H<sub>2</sub>O (2.15 g, 3.78 mmol) were dissolved in 50 mL of distilled water under sonication. Then the solution was added dropwise into the Graphene oxide suspension and stirred. The obtained solution was slowly basified with aqueous NH<sub>4</sub>OH (25%, 40 mL) up to pH~10 and was heated at 68 °C for 2 h. Finally, the Fe<sub>3</sub>O<sub>4</sub>/Graphene oxide nanocomposite was separated from the mixture using an external magnet, washed three times with ethanol and distilled water respectively and dried at 65 °C for 12 h.

## 2.3. Preparation of Fe<sub>3</sub>O<sub>4</sub>/Graphene Oxide/Pr-NH<sub>2</sub>

The obtained  $Fe_3O_4/Graphene$  oxide nanoparticles (2 g) were dispersed in EtOH (140 mL). Then, 3-aminopropyltriethoxysilane (APTES) (4 mL) was added and the mixture was sonicated for 1 h. After that, the reaction mixture was stirred under N<sub>2</sub> atmosphere (70 °C, 20 h). The desired product was collected using a permanent magnet, washed with distilled water and ethanol and dried (60 °C, a daytime).

# 2.4. Preparation of Fe<sub>3</sub>O<sub>4</sub>/Graphene Oxide/Pr–NH<sub>2</sub>–Cu<sup>II</sup>

Finally, for the preparation of  $Fe_3O_4/Graphene oxide/Pr-NH_2-Cu^{II}$ ,  $Cu(OAc)_2 \cdot 4H_2O$  (1 mmol) was added to a suspension of  $Fe_3O_4/Graphene$  oxide/Pr-NH<sub>2</sub> nanoparticles (1 g) in ethanol (25 mL). The mixture was refluxed for 20 h. The final product ( $Fe_3O_4/Graphene$  oxide/Pr-NH<sub>2</sub>-Cu<sup>II</sup>) was separated by permanent magnet, washed with ethanol and dried at 50 °C.

#### 2.5. Catalytic Reduction of 4-Nitrophenol

To investigate the catalytic reduction of 4-nitrophenol, NaBH<sub>4</sub> (0.01 g) was added to a 20 ppm 4-nitrophenol aqueous solution (20 mL). Then 0.01 g catalyst was added and the mixture was allowed to stir at room temperature until the deep yellow color of the solution turned colorless. UV-Vis spectroscopy was used to monitor the reaction progress. Upon completion of the reaction, the catalyst was simply separated from the reaction mixture using a

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permanent magnet, washed several times with ethanol and deionized water and dried for the next cycle.

# 3. RESULTS AND DISCUSSION

#### 3.1. Catalyst Characterization

The size and morphology of particles in the prepared catalyst was evaluated using FE-SEM (Fig. 1). Based on this technique the catalyst is as granule nanoparticles with the size distribution ranged from 18–28 nm. The EDX spectrum of the catalyst is presented in Figure 2, which indicated the presence of all of the expected elements (C, Fe, O, Si, N, and Cu) and also confirms that copper (II) complex was immobilized on the Fe<sub>3</sub>O<sub>4</sub>/Graphene oxide/Pr– NH<sub>2</sub>. The actual amount of Cu in prepared catalyst was determined using inductively coupled plasma-optical emission spectrometry (ICP-OES). This analysis indicated that the weight percentage of Cu was 6.3%.

Figure 3 shows the magnetization hysteresis curves for  $Fe_3O_4/Graphene$  oxide nanoparticles (curve a) and the synthesized catalyst (curve b). As can be seen, the saturation magnetization ( $M_s$ ) of the  $Fe_3O_4/Graphene$  oxide nanoparticles was about 29.63 emu g<sup>-1</sup>, which decreased to 26.92 emu g<sup>-1</sup> for  $Fe_3O_4/Graphene$  oxide/Pr–NH<sub>2</sub>–Cu<sup>II</sup>. However, it was still large enough for magnetic separation. Thus, after the end of the reaction, the catalyst could be easily collected by a permanent magnetic from the reaction medium. IP: 91.200.81.81 On: M



Figure 1. FE-SEM image of Fe<sub>3</sub>O<sub>4</sub>/graphene oxide/Pr-NH<sub>2</sub>-Cu<sup>II</sup>.



Figure 2. EDX spectrum of Fe<sub>3</sub>O<sub>4</sub>/graphene oxide/Pr-NH<sub>2</sub>-Cu<sup>II</sup>.

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Figure 3. Magnetization curves of (a)  $Fe_3O_4$ /graphene oxide and (b)  $Fe_3O_4$ /graphene oxide/Pr–NH<sub>2</sub>–Cu<sup>II</sup>.

X-ray diffraction (XRD) analysis was performed in order to determine the phase structure of Fe<sub>3</sub>O<sub>4</sub>/Graphene oxide/Pr–NH<sub>2</sub>–Cu<sup>II</sup> (Fig. 4). In XRD analysis, the diffraction peaks at  $2\theta = 30.31^{\circ}$ ,  $35.67^{\circ}$ ,  $43.28^{\circ}$ ,  $53.75^{\circ}$ ,  $57.30^{\circ}$ , and  $62.93^{\circ}$  can be indexed to (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) planes of Fe<sub>3</sub>O<sub>4</sub>-NPs in the cubic phase (JCPDS 89-2355). The pure Graphene oxide shows a sharp characteristic peak at  $2\theta = 11.28$ which can be attributed to the (0 0 1) plane of Graphene oxide. However, no diffraction peak related to Graphene oxide is observable for the obtained XRD spectrum of Fe<sub>3</sub>O<sub>4</sub>/Graphene oxide/Pr–NH<sub>2</sub>–Cu<sup>II</sup>, probably because

the layer stacking of the Graphene oxide sheets were destroyed by the loading of  $Fe_3O_4$ -NPs [37]. The average nanoparticel diameter of the prepared catalyst was calculated about 12 nm from the XRD results using the Debye Scherrer formula.

The FT-IR spectra of  $Fe_3O_4/Graphene$  oxide and  $Fe_3O_4/Graphene$  oxide/Pr– $NH_2$ – $Cu^{II}$  are shown in Figure 5. These spectra show absorption bands at 443 and 584 cm<sup>-1</sup>, which are attributed to the vibrational frequency of Fe–O bond. In the case of  $Fe_3O_4/Graphene$  oxide,



Figure 4. The XRD pattern of Fe<sub>3</sub>O<sub>4</sub>/graphene oxide/Pr-NH<sub>2</sub>-Cu<sup>II</sup>.



**Figure 5.** FT-IR spectra of (a)  $Fe_3O_4$ /graphene oxide and (b)  $Fe_3O_4$ /graphene oxide/Pr–NH<sub>2</sub>–Cu<sup>II</sup>.

the broad band observed at around 3400 cm<sup>-1</sup> is related to the presence of hydroxyl groups of Graphene oxide and Fe<sub>3</sub>O<sub>4</sub>. The absorption bands at 1180, 1402, 1618, and 1711 cm<sup>-1</sup> can be attributed to C–O (epoxy group), C–OH (carboxyl group), C=C, and C=O stretching vibrations (carboxyl group) of graphene oxide, respectively. The addition of APTES to the Fe<sub>3</sub>O<sub>4</sub>/Graphene oxide is confirmed by the new peaks at 2927, 2863, 1073 and 1127 cm<sup>-1</sup> that are correspond to the symmetric and asymmetric stretching vibrations of C–H bonds and Si–O stretching vibrations [38]. The presence of Cu(OAc)<sub>2</sub> in the catalyst is confirmed by the absorption bands at 1462, 1581 and 1725 cm<sup>-1</sup> that are related to asymmetric and symmetric stretching vibrations of acetate ions and C=O stretching vibration. The peak at 428 cm<sup>-1</sup> related to



Figure 6. UV-visible spectrum of the 4-nitrophenol aqueous solution.

Cu–NH<sub>2</sub> cannot be seen in the FT-IR spectrum because it is covered by the Fe–O stretching vibrations [39].

## 3.2. Catalytic Activity

After synthesis and characterization of  $Fe_3O_4$ /Graphene oxide/Pr–NH<sub>2</sub>–Cu<sup>II</sup> nanocomposite, its catalytic activity was investigated in the reduction of 4-nitrophenol in the presence of an excess amount of NaBH<sub>4</sub> as the mild reducing agent in the aqueous solution (Scheme 1).

It is well documented that  $NaBH_4$  as the source of hydrogen, does not reduce nitro group alone under ordinary conditions [40] and requires to associate with an adequate amount of catalyst. So, in order to demonstrate the necessity of using a catalytic system for the conversion of 4-nitrophenol to 4-aminophenol, the reduction procedure was conducted in the absence of the synthesized catalyst at first. The chemical reduction of 4-nitrophenol was easily studied using UV-Vis spectroscopy. As observed in



Scheme 1. Preparation process and application of Fe<sub>3</sub>O<sub>4</sub>/Graphene oxide/Pr-NH<sub>2</sub>-Cu<sup>II</sup> in the reduction of 4-nitrophenol.



Scheme 2. The catalytic reduction of the 4-nitrophenol to 4-aminophen.

Figure 6, 4-nitrophenol aqueous solution shows a strong absorption peak at 317 nm. Upon the addition of NaBH<sub>4</sub>, the absorption shows red-shift to 400 nm with a color change from pale yellow to dark yellow because of the formation of 4-nitrophenolate ions under alkaline conditions. The maximum absorption peak remained unchanged at 400 nm even after two days, which revealed the reduction of 4-nitrophenol will not proceed only in the presence of NaBH<sub>4</sub>. However, after the addition of a suitable amount of the Fe<sub>3</sub>O<sub>4</sub>/Graphene oxide/Pr-NH<sub>2</sub>-Cu<sup>II</sup> nanocomposite to this solution, the peak at 400 nm gradually dropped in intensity and a new peak related to the formation of 4-aminophenol appeared as a shoulder at 300 nm (Scheme 2, Fig. 7). After about 4 min the whole peak at 400 nm disappeared and the yellow color of the solution altered to colorless which shows the complete conversion of 4-nitrophenol to 4-aminophenol.

In the catalytic reduction of 4-nitrophenol with NaBH<sub>4</sub> for the r in the presence of Fe<sub>3</sub>O<sub>4</sub>/Graphene oxide/Pr–NH<sub>2</sub>–Cu<sup>II</sup>, as an electron transfer procedure [[41]], at first, the lent cata 4-nitrophenol and BH<sub>4</sub><sup>-</sup> ion are both absorbed on the surface of the catalyst by  $\pi - \pi$  stacking interactions. After that, an electron transfer process happens from BH<sub>4</sub><sup>-</sup> to 4-nitrophenol ions. Finally, the 4-aminophenol was desorbed from the surface of the catalyst. **4.** COI

The reusability of a catalyst is very worthwhile from the viewpoint of green chemistry and commercial applications. To evaluate this issue, after completion of the reaction, monitored by UV-Vis spectroscopy, the catalyst was separated from the reaction medium simply by a permanent



Figure 7. UV-visible spectra of the 4-nitrophenol aqueous solution reduced by  $NaBH_4$  in the presence of  $Fe_3O_4$ /graphene oxide/Pr-NH<sub>2</sub>-Cu<sup>II</sup>.

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**Table I.** Comparison of various catalysts in the reduction of 4-nitrophenol by NaBH<sub>4</sub>.

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Entry	Catalyst	Catalyst loading	Conversion time (min)	Ref.
1	Au/graphene hydrogel	0.1 mg	12	[42]
2	Au@TpPa-1	20 mg	13	[43]
3	Au–Ag bimetallic NPs supported on LDH	20 µL, 1 mg	30	[15]
4	Cu microspheres	5 mg	18	[44]
5	Ag/KCC-1	20 $\mu$ L, 10 mg mL <sup>-1</sup>	8.5	[45]
6	Pd@HCS	3 mg	5	[46]
7	Hypercross-linked porous PS/IL networks	150 mg	10	[47]
8	Ni-PVAm/SBA-15	12 mg	85	[48]
9	Fe <sub>3</sub> O <sub>4</sub> /graphene oxide/Pr-NH <sub>2</sub> -Cu <sup>II</sup>	10 mg	4	[This work]

magnet, washed several times with ethyl acetate, dried and reused for the consecutive runs. For this experiment, the catalyst was reused at least for five consecutive runs without significant change in its catalytic activity.

The applicability and efficiency of the prepared catalyst was compared with some other published works for the reduction of 4-nitrophenol by NaBH<sub>4</sub>. As can be seen, Fe<sub>3</sub>O<sub>4</sub>/Graphene oxide/Pr–NH<sub>2</sub>–Cu<sup>II</sup> has an excellent catalytic activity for the reduction of 4-nitrophenol to 4-aninophenol (Table I).

#### 4. CONCLUSION

In summary, we have reported the synthesis and characterization of a novel nanocomposite formulated as  $Fe_3O_4/Graphene \text{ oxide/Pr-NH}_2-Cu^{II}$  as an efficacious and environmentally benign catalyst for the reduction of 4-nitrophenol to 4-aminophenol with NaBH<sub>4</sub> in aqueous solution. The advantages of this catalytic system are ease of preparation, short time of the reaction, high catalytic activity and the use of commercially available, cheap and eco-friendly materials. Also, the magnetic nature of this catalyst allows its easy separation from the reaction medium by an external magnet. The catalyst can be reused five times without noticeable changes of its catalytic activity. This catalytic system may also be used in the reduction of other toxic organic pollutants.

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