

Article

Fabrication of Copper(II)-Coated Magnetic Core-Shell Nanoparticles $\text{Fe}_3\text{O}_4@\text{SiO}_2$: An Effective and Recoverable Catalyst for Reduction/Degradation of Environmental Pollutants

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Abstract: In this work, we report the synthesis of a magnetically recoverable catalyst through immobilizing copper (II) over the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles (NPs) surface [$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}$] (L = pyridine-4-carbaldehyde thiosemicarbazide). Accordingly, synthesized catalysts were determined and characterized by energy dispersive X-ray spectrometry (EDS), X-ray diffraction (XRD), Fourier transforms infrared spectroscopy (FT-IR), vibrating sample magnetometer (VSM), field emission scanning electron microscopy (FESEM), and thermogravimetric-differential thermal analysis (TG-DTA) procedures. The [$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}$] was used for the reduction of Cr(VI), 4-nitrophenol (4-NP) and organic dyes such as Congo Red (CR) and methylene blue (MB) in aqueous media. Catalytic performance studies showed that the [$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}$] has excellent activity toward reduction reactions under mild conditions. Remarkable attributes of this method are high efficiency, removal of a homogeneous catalyst, easy recovery from the reaction mixture, and uncomplicated route. The amount of activity in this catalytic system was almost constant after several stages of recovery and reuse. The results show that the catalyst was easily separated and retained 83% of its efficiency after five cycles without considerable loss of activity and stability.

Keywords: copper nanocomplex; core/shell structure; Fe_3O_4 nanoparticles; environmental pollutant; dye degradation



Citation: Dadashi, J.; Khaleghian, M.; Mirtamizdoust, B.; Hanifehpour, Y.; Joo, S.W. Fabrication of Copper(II)-Coated Magnetic Core-Shell Nanoparticles $\text{Fe}_3\text{O}_4@\text{SiO}_2$: An Effective and Recoverable Catalyst for Reduction/Degradation of Environmental Pollutants. *Crystals* **2022**, *12*, 862. <https://doi.org/10.3390/cryst12060862>

Academic Editors: Abdullah Mohamed Asiri and Bo Chen

Received: 24 March 2022

Accepted: 14 June 2022

Published: 18 June 2022

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1. Introduction

Nitroarene compounds and toxic dyes are the main pollutants in wastewater of various industries, including textile and dyeing industries, explosives production, cosmetics production, food industry, pharmaceutical, and paper industries [1,2]. These synthetic organic compounds are highly toxic and one of the most resistant pollutants in the environment. Moreover, they have adverse effects on the central nervous system, liver, and blood of animals and humans. Developing an effective and straightforward method for the degradation of non-biodegradable pollutants into non-hazardous products is one of the severe challenges in environmental studies [3,4]. Among the various methods, chemical reduction in the presence of a reducing agent is an economical and effective method for removing dyes [5]. For example, 4-aminophenol, which is the product of 4-nitrophenol reduction, is a valuable and essential compound [6]. This compound is widely used as the main intermediate in the pharmaceutical and dyeing industries [7]. However, the chemical reduction of dyes is a prolonged process, and the use of a suitable catalyst is a serious need for the development of this method.

Among the heavy metals in industrial effluents, chromium is one of the most critical pollutants in water and wastewater, which is necessary to remove from polluted water. Improper use and discharge of effluents from these industries to the environment will pose many risks to humans and ecosystems [8]. Chromium is one of the most widely used industrial elements, which mainly exists in the form of trivalent and hexavalent chromium in the environment [9]. Cr(VI) is highly toxic due to the formation of free radicals in cells and has been identified by many reputable international organizations as the cause of lung cancer [10]. Other side effects of Cr(VI) in the body include perforation of the septum, skin allergies, dermatitis and disorders of the stomach, liver, and kidneys [11,12]. Cr(VI) is highly soluble in water and can form divalent anions such as chromate (CrO_4^{2-}), dichromate ($\text{Cr}_2\text{O}_7^{2-}$), and hydrogen chromate (HCrO_4^-) at different pHs [13,14].

Various catalysts have been synthesized and used to facilitate the conversion of reactants to final products [15]. Generally, there are two types of catalysts; the homogeneous catalyst is a single atom, ion, or molecule and is in the same phase as the reactants. In other words, homogeneous catalyst particles can be dissolved in the reaction mixture easily. This catalyst is consumed in the reaction and produced. The advantages of this type of catalyst are very high activity, selectivity, and good efficiency. Improvements in the performance of homogeneous catalysts can be achieved by attaching different organic and inorganic groups to the parent particle. Despite the high efficiency of the homogeneous catalysts, the main problem with this type of catalyst is that after the reaction is complete, separating the dissolved catalyst from the final mixture is not an easy task. This problem is a significant challenge, especially when the catalyst is consumed in small amounts [16]. The second type of catalyst is the heterogeneous catalyst, which are in another phase with the reactants, unlike the homogeneous catalyst. For example, the reactants are in the liquid phase (in solution), but the catalyst is solid [17]. The size and properties of the heterogeneous catalyst particles are such that they do not dissolve easily in the reaction medium. Unlike homogeneous catalysts, heterogeneous catalysts are easily (with less cost, time, and materials) separated from the reaction mixture and do not cause product impurities. In order to compensate for the lack of active surface in such compounds, it is necessary to use a support in the role of the catalyst support [18]. The substrate is usually a porous structure with a high active surface. Industry uses heterogeneous processes more than homogeneous catalysts in the sight of the simple workup, ease of handling, and separations [19]. Eliminating environmental pollution by selecting an eco-friendly and effective method is one of the most critical tasks. Several nanoparticles with specific physical and chemical properties may serve as remediation compounds for the environment. The removal or reduction of organic pollutants can be accomplished in many ways, including biological, physical, and chemical methods. Some of these approaches, such as adsorption, filtration, sorbents, photocatalysis, and chemical reactions, are not useful and practical owing to their disadvantages such as higher cost, energy consumption, and the production of dangerous by-products [20]. Metal-organic frameworks (MOFs) have many potential applications, but their intrinsic nano/micro powder nature presents challenges during recovery and deployment. Despite significant efforts made to develop solid supports for MOFs, they are still limited by the poor loading stability and durability of MOFs [21]. In recent years, iron-based metal-organic frameworks (Fe-MOFs) have been considered competitive catalyst candidates for the removal of organic pollutants through advanced oxidation processes (AOPs) because of their unique porous architectures and tunable active sites. However, little is known about the role of the synergetic relationship between porous architecture and active site exposure of Fe-MOFs on catalysis for AOPs yet [22]. In recent decades, magnetic nanoparticles (MNPs) have gained growing attention due to their facile recovery, unique magnetic responsivity, high magnetic susceptibility, biocompatibility, low toxicity, and large surface area [23]. Heterogeneous catalysts are mainly used in the form of nanoparticles regarding their larger available catalytic surface. One of the most useful procedures for the preparation of heterogeneous nano-catalysts is to immobilize complexes on solid bases such as metal and metal oxides. Magnetic iron oxide nanoparticles (MNPs Fe_3O_4) have received

a big deal of interest within metal oxide nanoparticles (NPs), probably because of their special applications [24,25]. Iron oxides have good magnetic properties compared to other magnetic nanoparticles and, on the other hand, show high stability against degradation. By choosing a suitable synthesis method, the size, shape, surface coating, and colloidal stability of magnetic nanoparticles can be optimally controlled. Nowadays, the use of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core-shell composite nanoparticles has been developed as efficient catalysts for organic reactions [26–31]. They also can be used in various research fields such as data storage [32], gene manipulation [33,34], drug delivery [35–38], immunoassay [39,40], magnetic bio separation [41–43], magnetic resonance imaging (MRI) [44], environmental remediation [45–47], biomedicine [48–50], and catalysts [51–54].

Despite all related research, the successful synthesis of a copper(II) complex by immobilizing the synthesized pyridine-4-carbaldehyde thiosemicarbazide ligand (L) on the magnetite nanoparticles coated with silica ($\text{Fe}_3\text{O}_4@\text{SiO}_2$) surface and its use as a magnetically reusable catalyst for reduction of Cr(VI), MB, CR, and 4-NP in the presence of NaBH_4 have not been reported. In this research, copper(II) complex was processed through immobilizing the synthesized pyridine-4-carbaldehyde thiosemicarbazide ligand (L), on the magnetite nanoparticles coated with silica ($\text{Fe}_3\text{O}_4@\text{SiO}_2$) surface as a new, and magnetically reusable catalyst. Moreover, the catalytic activity of $[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$ was assessed for reducing Cr(VI), MB, CR, and 4-NP within an aqueous medium.

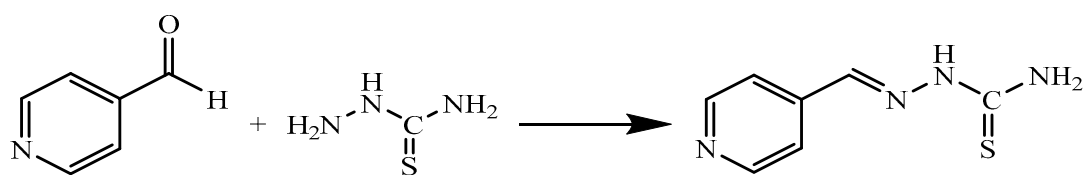
2. Experimental

2.1. Materials and Instruments

The chemical reagents and solvents used in this research have a high purity percentage and were purchased from reputable companies Aldrich (Seoul, Korea) and Merckb (Seoul, Korea). The list of materials and solvents used is as follows: pyridine-4-carbaldehyde Sigma-Aldrich 97%, thiosemicarbazide 99%, Fe_3O_4 95%, TEOS $\geq 99\%$, (3-chloropropyl) trimethoxysilane 95%, $\text{K}_2\text{CO}_3 \geq 99\%$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O} \geq 97\%$, 4-nitrophenol $\geq 99\%$, methylene blue, Congo Red, $\text{K}_2\text{Cr}_2\text{O}_7 \geq 99\%$, HCOOH (88%), $\text{NaBH}_4 \geq 98\%$, ethanol 98%, acetic acid $\geq 99\%$, $\text{NH}_3 \geq 99\%$, dry toluene 99.8%, and DMF $\geq 99\%$. The Shimadzu 800IR 100FT-IR (Kyoto, Japan) spectrometer was used to record the FT-IR spectra. The Hitachi U-2900 double-beam spectrophotometer with wavelengths in the range of 200–800 nm was used to obtain UV-Visible spectra. The TESCAN4992 device (Brno, Czech Republic) was used to perform an energy-dispersive X-ray (EDX) analysis. An accurate magnetometer of Iran Kavir VSMs (Kashan, Iran) was used to perform vibrating sample magnetometer measurements. Nanocatalyst's morphology was studied by applying FE-SEM images (ZEISS Sigma VP, Oberkochen, Germany). STA 504 analyzer (New Castle, USA) was applied in the argon atmosphere to perform thermal analysis (TG-DTG). Powder X-ray diffraction (XRD) patterns of the sample were examined utilizing a PANalytical X-PERT-PRO MPD diffractometer (Malvern, UK).

2.2. Preparation of Pyridine-4-Carbaldehyde Thiosemicarbazide Ligand (L)

In a 100 mL flask, 0.752 g of pyridine-4-carbaldehyde was dissolved in ethanol 98% percent, and one drop of acetic acid was added. Shortly after, 0.636 g of thiosemicarbazide 99% was gradually added. The color of the solution changes to yellow as soon as the amine is introduced, indicating the formation of a Schiff base ligand. The solution was then refluxed for 12 h with stirring. The crystals were then filtered and washed with a bit of cold ethanol (4 °C). The L ligand is depicted in Scheme 1 [55–57]. Schemes S1 and S2 display the Enol-ketone tautomerization and coordination method of L Schiff base ligand. Table S1 provides some physical characteristics of L ligand. Also, see Figure S1 as FT-IR spectrum of L ligand.



Scheme 1. Molecular structure of L ligand.

2.3. $[Fe_3O_4@SiO_2-L-Cu(II)]$ Catalyst Synthesis Procedure

The $[Fe_3O_4@SiO_2-L-Cu(II)]$ combination was synthesized using the following technique. A total of 4.0 g Fe_3O_4 , 230.0 mL ethanol, 10.0 mL NH_3 , 80.0 mL water, and 6.0 mL tetraethylorthosilicate (TEOS) were vigorously agitated for 12 h under reflux conditions before being ultrasonicated for 30 min in the first stage. About 300.0 mL dry toluene and 3.0 mmol (3-chloropropyl) trimethoxysilane were added to 5.0 g $Fe_3O_4@SiO_2$ and refluxed for 24 h at 110 °C in the following stage. An external magnetic field was used to assemble the precipitate, which was then washed with dry toluene and deuterium-depleted water (DDW) before being oven-dried for 6 h at 80 °C. After that, 2.0 g of $Fe_3O_4@SiO_2-(CH_2)_3Cl$, 0.9 g of L (5.0 mmol), 50.0 mL of dimethylformamide, and 0.691 g of K_2CO_3 (5.0 mmol) were combined and refluxed for 24 h to make the $Fe_3O_4@SiO_2-(CH_2)_3-L$. An external magnetic field was used to build the solid product, which was then scoured with DMF and parched. Finally, 1.0 g of the $Fe_3O_4@SiO_2-L-Cu(II)$ complex was made by adding 0.5 g of $CuCl_2 \cdot 2H_2O$ and 50.0 mL of ethanol to 0.5 g of $CuCl_2 \cdot 2H_2O$ and stirring the reaction mixture vigorously in refluxing EtOH for 24 h.

2.4. Catalytic Activity of $[Fe_3O_4@SiO_2-L-Cu(II)]$ for 4-NP Reduction

Different amounts of $[Fe_3O_4@SiO_2-L-Cu(II)]$ (7.0, 5.0, 3.0 mg) were added to 25 mL of 4-NP aqueous solution to evaluate catalytic activity (2.5 mM). Following that, 25 mL of newly prepared sodium tetrahydroborate aqueous solution (0.25 M) was added, and the mixture was stirred at room temperature for 30 min (r.t). A UV-Vis spectrophotometer (Agilent, Santa Clara, USA) was used to measure the solution's absorbance during the process. The soluble yellow tint gradually fades, indicating that 4-AP has been produced from 4-NP.

2.5. Catalytic Degradation of CR and MB by Employing $[Fe_3O_4@SiO_2-L-Cu(II)]$ Complex

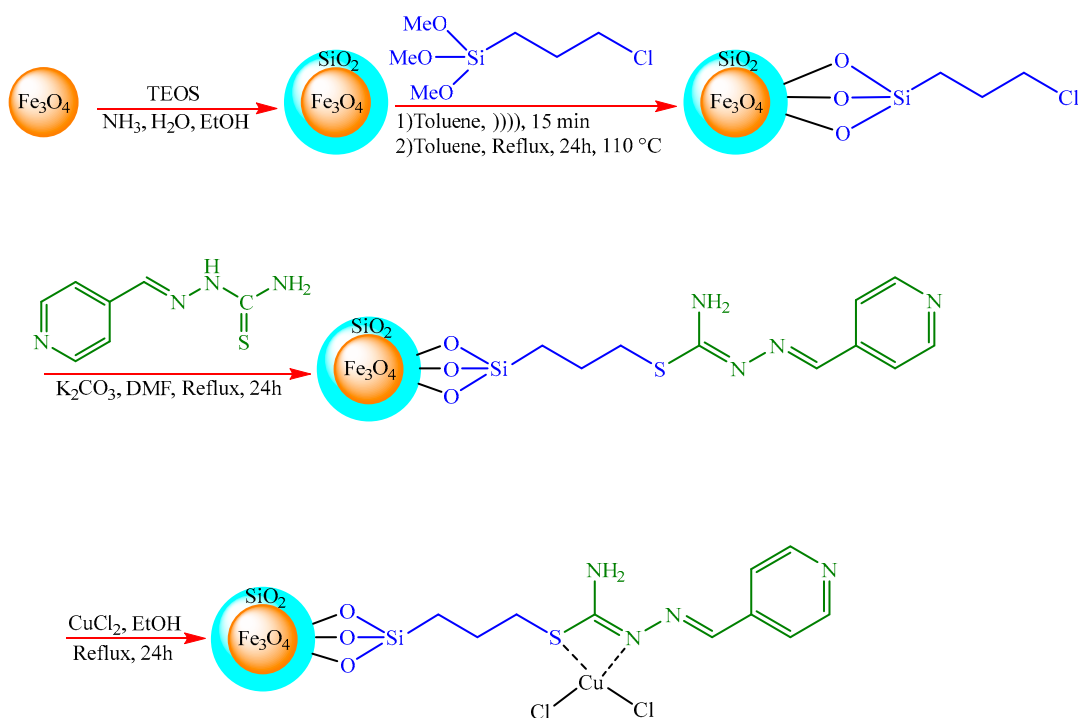
Methylene blue (MB) and Congo Red (CR), two water-soluble organic dyes, were chosen as samples for reduction using $[Fe_3O_4@SiO_2-L-Cu(II)]$ in the presence of the reducing agent sodium borohydride. About 7.0 mg of the produced catalyst was injected into 25 mL of aqueous dye solution (3.1×10^{-5} M) in a typical reduction operation. The mixture was then added to 25 mL of freshly prepared sodium tetrahydroborate solution (0.025 M) and agitated at room temperature. The reaction was carried out using UV-Vis spectroscopy. After the reaction, an external magnetic field was used to extract $[Fe_3O_4@SiO_2-L-Cu(II)]$, which was then rinsed with doubly distilled H_2O and reused.

2.6. Catalytic Activity of $[Fe_3O_4@SiO_2-L-Cu(II)]$ for Cr(VI) Reduction

The catalyst's reductive capacity was tested by reducing Cr(VI) to Cr(III). At 50 °C, 7.0 mg of $[Fe_3O_4@SiO_2-L-Cu(II)]$ was added to 25 mL of 3.4×10^{-3} M $K_2Cr_2O_7$ solution and 1.0 mL HCO_2H (88%) under constant stirring. The reduction process was monitored using UV-Vis spectroscopy. The nano-catalyst was easily detached and re-used when the yellow tint of the reaction media vanished.

3. Results and Discussion

Scheme 2 shows the stages in the synthesis of $[Fe_3O_4@SiO_2-L-Cu(II)]$. The synthesized catalyst was characterized using EDS, FT-IR, VSM, TG-DTA, XRD, and FESEM.



Scheme 2. Preparing the $[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$.

The FT-IR spectra was used to confirm the coordination of the Cu atom by the L ligand and the immobilization of the complex on the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ surface (Figure 1). The absorption peaks of the Fe-O band in Fe_3O_4 MNPs were approximately 623 cm^{-1} . The Si-O bending, Si-O-Si stretching, and Si-O-Si bending in $\text{Fe}_3\text{O}_4@\text{SiO}_2$ are responsible for the absorption peaks at 458, 798, and 1096 cm^{-1} , respectively. Furthermore, the N-H stretching modes of the L ligand of the Fe_3O_4 NPs are seen in the absorption peaks around 3340 and 3390 cm^{-1} . The peak at 1626 is also linked to the C=N stretching band of the L ligand, indicating ligand grafting on the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ surface.

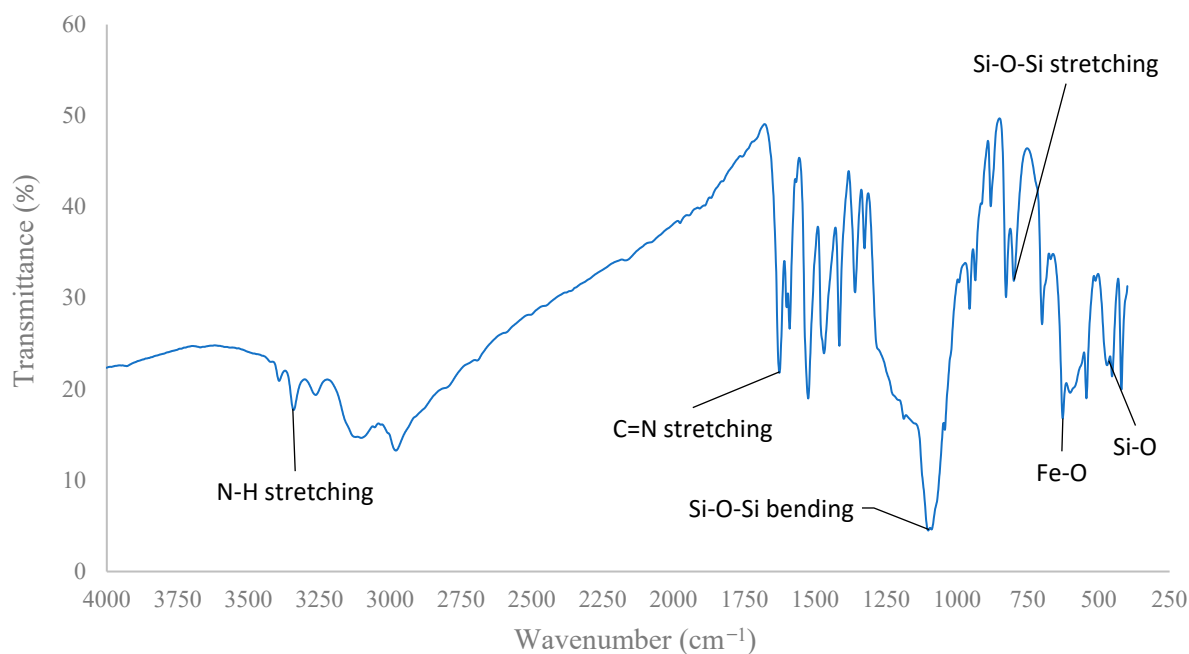


Figure 1. The FT-IR spectra of the $[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$ complex.

The phase and crystalline nature of $[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$ were evaluated by XRD analysis (Figure 2). As depicted in Figure 2, the XRD pattern of the catalyst demonstrated typical peaks at $2\theta = 29.2^\circ$, 35.56° , 41.25° , 56.34° , and 62.91° , which are attributed to (220), (311), (400), (422), and (440) crystal planes of the cubic crystalline Fe_3O_4 NPs, respectively (JCPDS file, File No. 19-0629), confirming the fabrication of magnetic nanocatalyst.

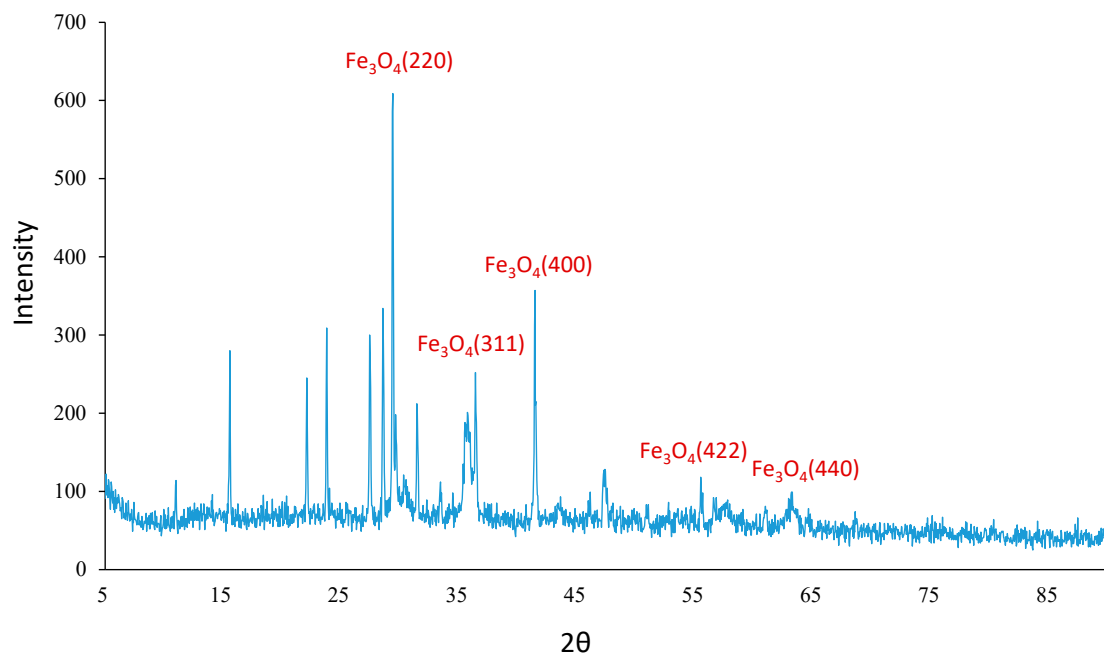


Figure 2. X-ray diffraction pattern of $[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$.

Vibration sample magnetometer (VSM) analysis was used to evaluate the magnetic properties of the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}$ complex at room temperature (Figure 3). The $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}$ complex has a lower saturation magnetization (M_s) than Fe_3O_4 MNPs. When the complex and SiO_2 were applied to the Fe_3O_4 MNPs surface, the saturation magnetization of the Fe_3O_4 core fell from around 60.0 emu g^{-1} to 21.0 emu g^{-1} , as seen in Figure 3.

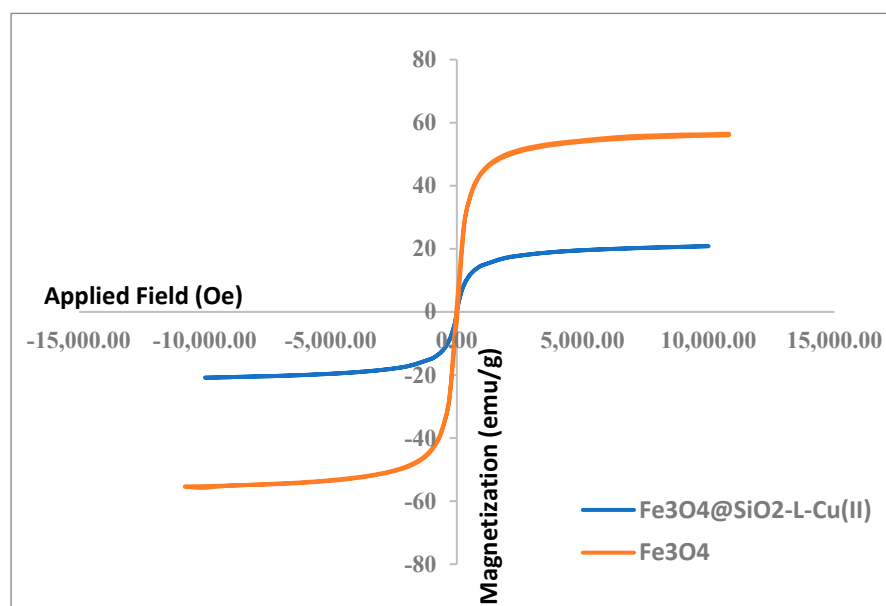


Figure 3. The magnetization curve for the magnetic nanocatalyst.

Chemical compositions of the $[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$ complex were also characterized using EDS. This examination confirmed that $[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$ included Fe, S, O, Cl, Si, and Cu, and that the Cu complex was coated on the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ surface, as shown in Figure 4.

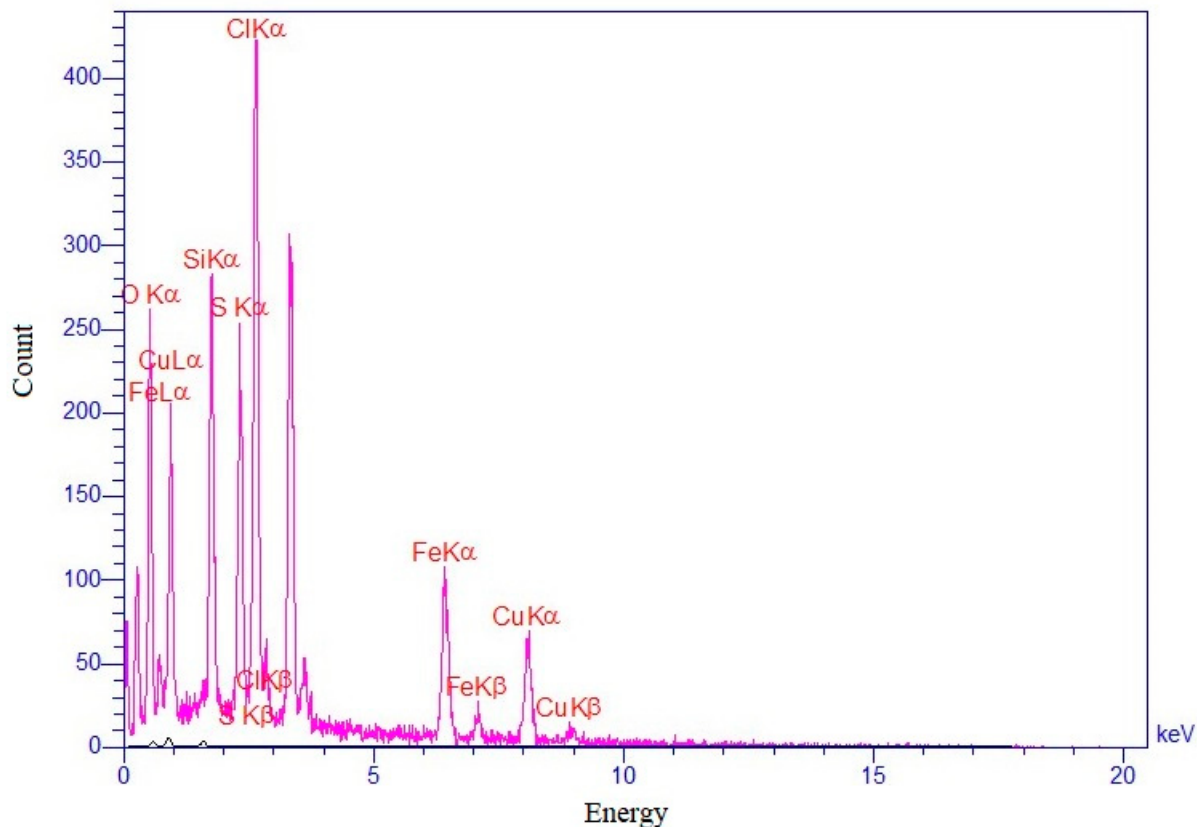


Figure 4. Energy dispersive X-ray spectrum of the $[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$.

Field emission scanning microscopy (FE-SEM) was used to examine the surface morphology of the produced nanocatalyst. The produced nanoparticles have a spherical form and are of varied sizes, less than 100 nm, according to FE-SEM analysis. Furthermore, $[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$ has a core-shell structure, as seen in Figure 5.

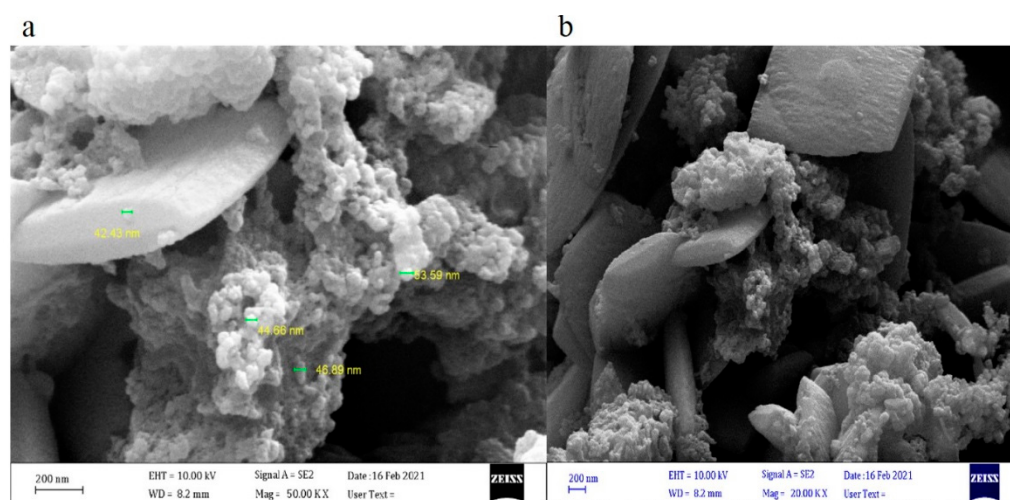


Figure 5. (a) and (b) Field emission scanning electron microscopy images of the $[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$ at different magnification.

At 100 °C, the weight loss is due to the removal of water or organic-solvents from the specimen; between 200 and 300 °C, the weight loss is due to the sequential cleavage of organic moieties; and between 400 and 500 °C, the weight loss is due to the disintegration of organic groups and prepared ligand. When the temperature rises above 800 °C, the catalyst disintegrates (Figure 6).

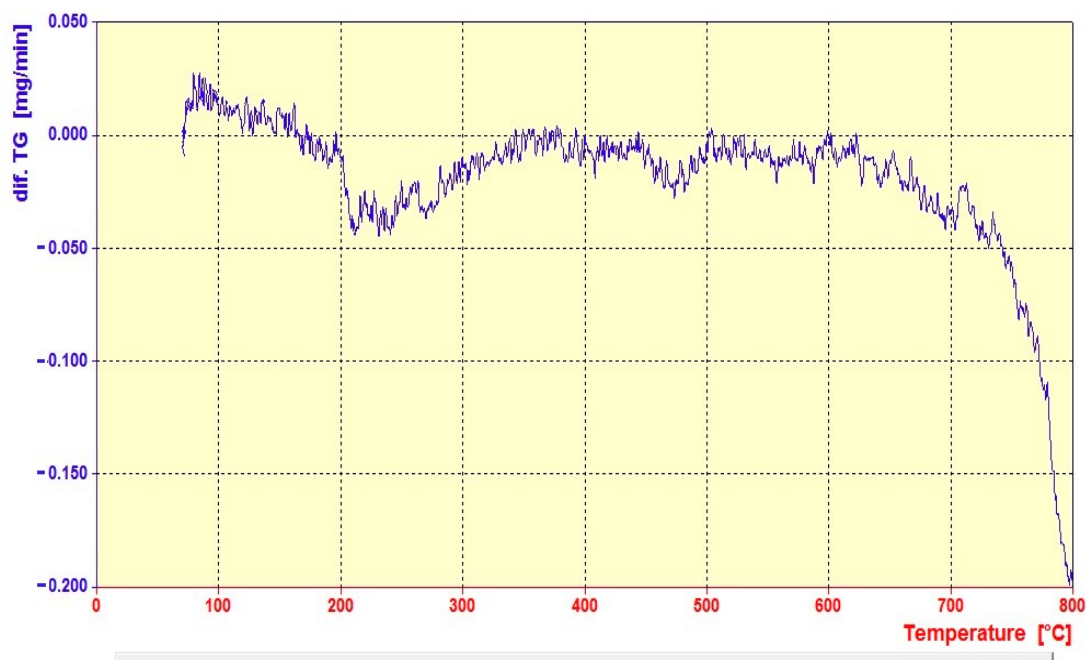


Figure 6. The thermogravimetric-differential thermal analysis data was determined for the magnetic nano-catalyst.

3.1. Catalytic Reduction of 4-NP by $[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$ Catalyst

In the presence of sodium tetrahydroborate, the catalytic activity of $[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$ was tested by reducing 4-nitrophenol to 4-aminophenol in water. The reduction occurs only when the catalyst is present, and it does not occur when there is no $[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$. The reaction times for the catalytic reduction of 4-nitrophenol in the presence of NaBH_4 and various catalyst values are shown in Table 1. According to the table, increasing the amount of catalyst and NaBH_4 speeds up the process. Despite the lack of a catalyst, the reduction technique took longer than 100 min to complete. With 7.0 mg of $[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$ and 100 equivalents NaBH_4 , the best result was obtained (Table 1, entry 5). Figure 7 shows the concentration changes of 4-nitrophenol over the reaction time.

Table 1. Optimization conditions for reduction of the 4-nitrophenol using synthesized catalyst at room temperature.

Entry	NaBH_4 (Equivalents)	Catalyst (mg)	Time
1	100	-	Not reaction
2	100	$\text{Fe}_3\text{O}_4@\text{SiO}_2$ (7.0)	Not reaction
3	100	$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L}$ (7.0)	Not reaction
4	-	$[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$ (7.0)	Not reaction
5	100	$[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$ (7.0)	114 s
6	79	$[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$ (7.0)	135 s
7	50	$[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$ (7.0)	192 s
8	100	$[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$ (5.0)	125 s
9	79	$[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$ (5.0)	159 s
10	50	$[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$ (3.0)	182 s
11	100	$[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$ (3.0)	140 s

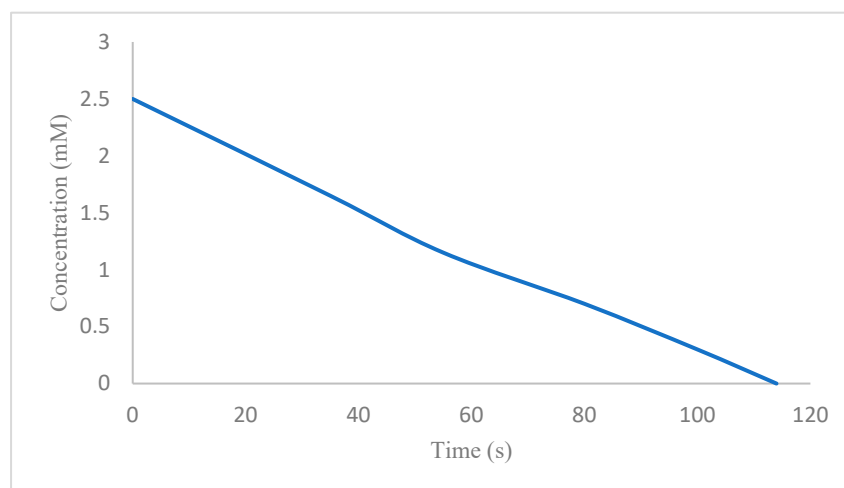
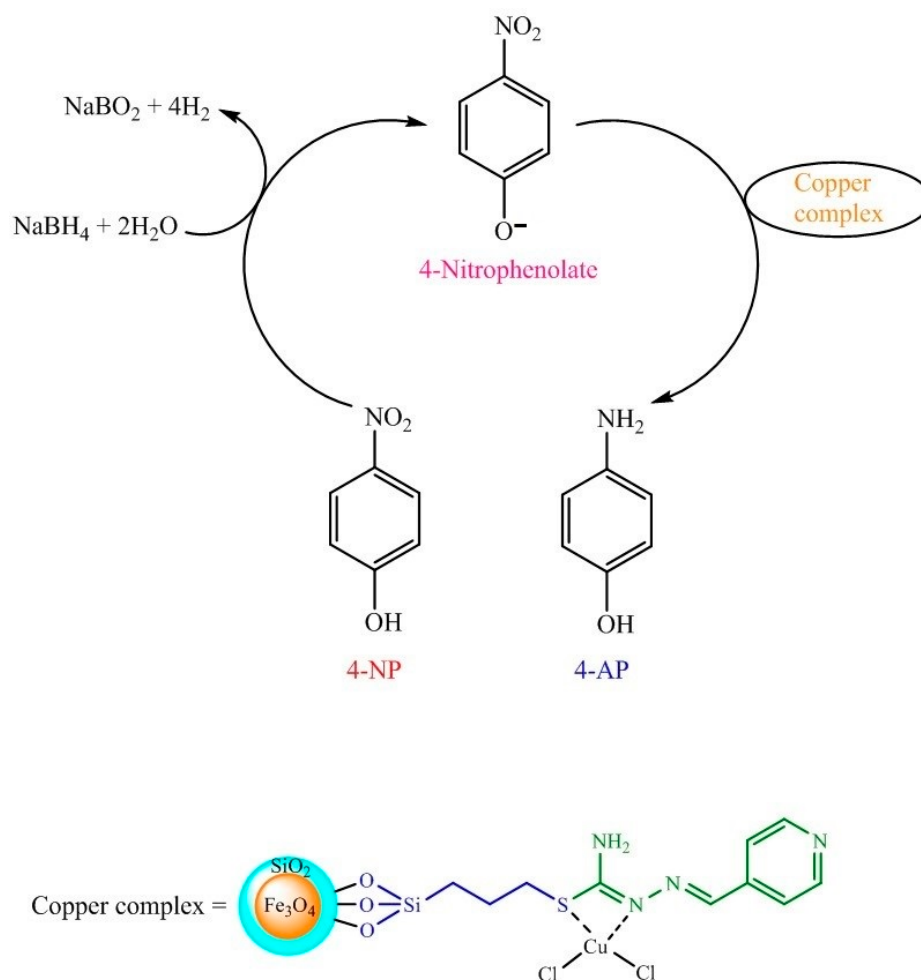


Figure 7. The concentration change of 4-nitrophenol over the reaction time.

The electron relay effects in the donor BH_4^- and acceptor nitro groups play an important role in the magnetic catalyst, as shown in Scheme 3. The reduction of 4-nitrophenol happens in two stages: first, diffusion of 4-NP and BH_4^- from aqueous solution to the catalyst's surface via stacking interactions, and second, electron transfer from BH_4^- to 4-AP mediated by the $[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$ surface.



Scheme 3. The reduction of 4-nitrophenol to 4-aminophenol applying $[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$.

The reduction of 4-nitrophenol to the 4-aminophenol procedure was monitored using the UV-Vis spectrum at r.t (Figure 8). The absorption peaks of 4-NP at 317 nm change to 400 nm after adding the sodium borohydride solution to the catalyst and 4-NP combination, resulting in the formation of 4-nitrophenolate ions. In the presence of $[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$, a new peak appeared at about 297 nm, showing that 4-aminophenol was produced from 4-nitrophenol.

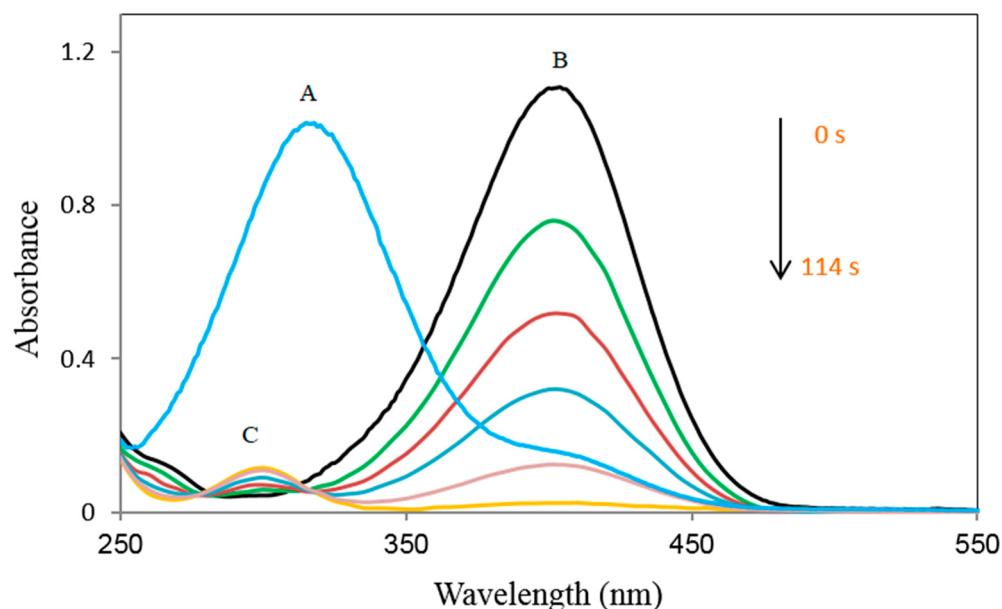
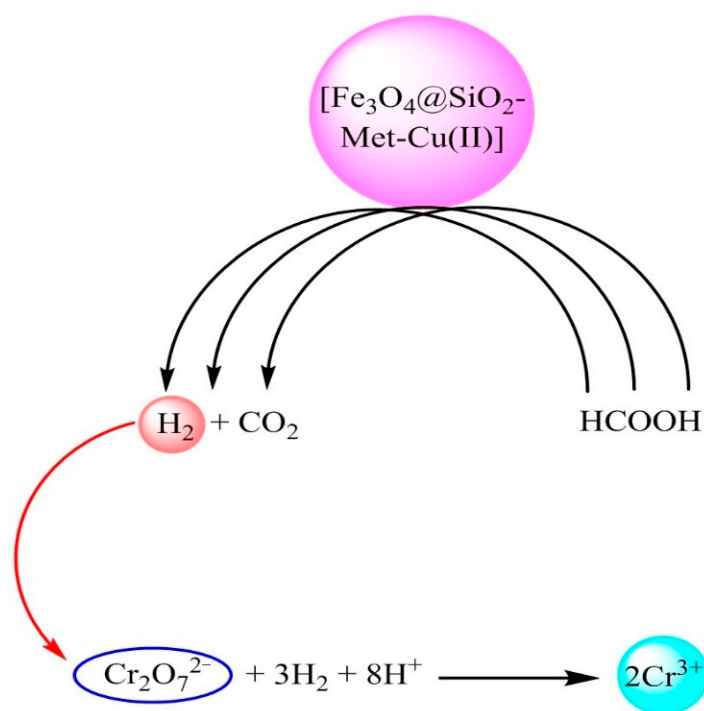


Figure 8. The UV-visible spectrum of the 4-nitrophenol reduced with NaBH_4 in $[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$. A: 4-NP, B: 4-nitrophenolate ion, C: 4-AP. Different colored lines created by various time of reaction from zero to 114 s.

3.2. Catalytic Reduction of Cr (VI) by $[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$

Because Cr(VI) is highly toxic to living beings, it should be eliminated as soon as possible before being released into the environment. The catalytic behavior of $[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$ in reducing chromium(VI) to chromium(III) was examined using the HCO_2H aqueous solution, similar to the previous findings. Hydrogen transfer from HCO_2H as an electron transfer from ligand (O) to Cr(VI) and a hydrogen donor to metal (chromium(VI)) was used to reduce chromium(VI) (Scheme 4). The HCO_2H is degraded onto the Cu(II) surface without creating the intermediated molecules, yielding CO_2 and H_2 as acceptable products.

We used UV-Vis absorption spectroscopy to monitor the reduction of the Cr(VI) protocol, which indicates a feature absorption peak of 350 nm (Figure 9). Figure 8 shows the reduction of chromium (VI) in an aqueous solution caused by $[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$ and HCO_2H at various time intervals. Table 2 summarizes and presents the experimental outcomes. The HCO_2H -mediated transfer of Cr(VI) did not reduce after 100 min with no catalyst (Table 2, entry 1). Within 11 min of adding $[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$, the HCO_2H -mediated reduction of chromium(VI) reduces, as evidenced by a change in color from yellow to colorless and the disappearance of the absorption band at 350 nm. With 7.0 mg of $[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$ and 1.0 mL of the aqueous HCO_2H solution, the best results were obtained (Table 2, entry 4). Figure 10 shows the concentration changes of Cr(VI) over the reaction time.



Scheme 4. The schematic reduction of Cr(VI) to Cr(III) utilizing magnetic nanocatalyst.

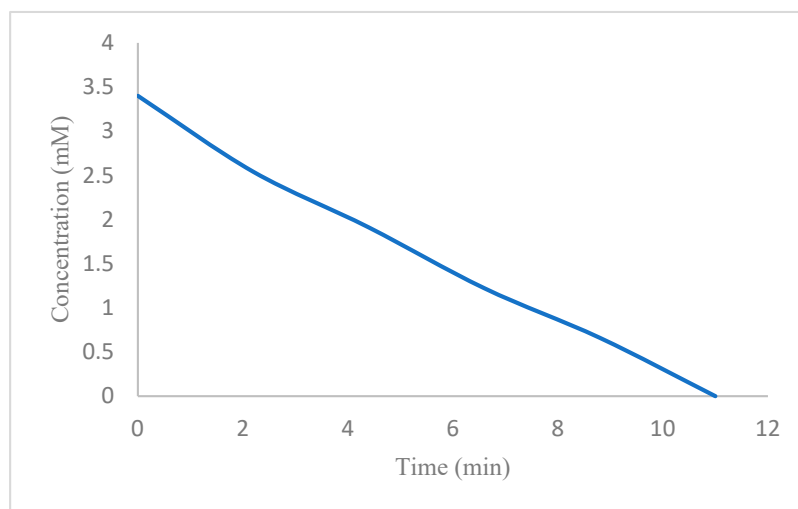


Figure 9. The concentration change of Cr(VI) over the reaction time.

Table 2. Optimizing conditions for the Cr(VI) reduction using $[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$ and HCOOH at 50 °C.

Entry	Formic Acid	Catalyst (mg)	Time
1	1.0 mL	-	No reaction
2	1.0 mL	$[\text{Fe}_3\text{O}_4@\text{SiO}_2]$ (7.0)	No reaction
3	1.0 mL	$[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L}]$ (7.0)	No reaction
4	1.0 mL	$[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$ (7.0)	11 min
5	1.0 mL	$[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$ (5.0)	19 min
6	1.0 mL	$[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$ (3.0)	29 min

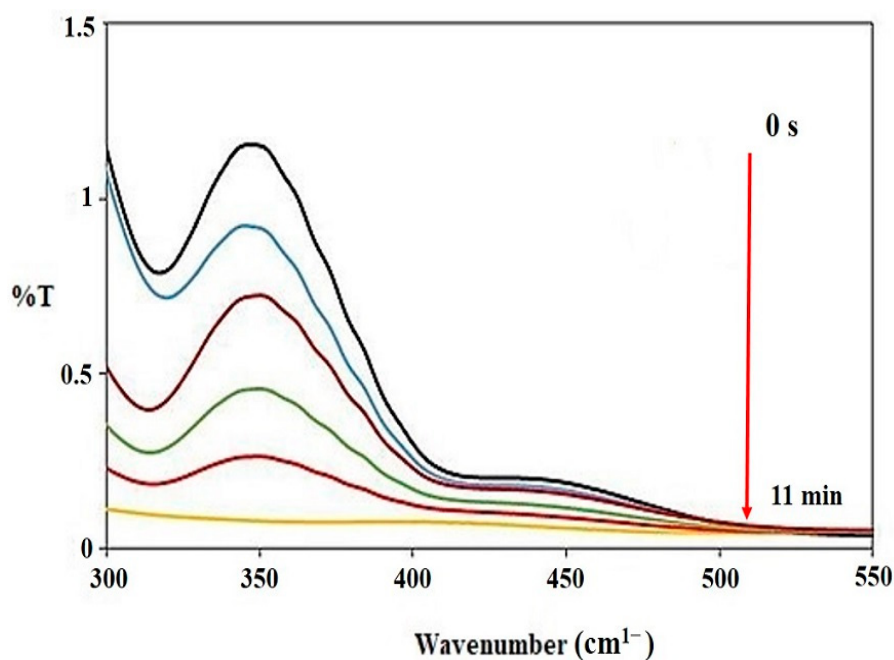


Figure 10. The Cr(VI) aqueous solution's UV-Vis spectra were utilizing HCOOH (1.0 mL) and $[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$. Different colored line created by various time of reaction from zero to 11 min.

3.3. Catalytic Reduction of MB and CR by Using and $[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$

The catalytic activity of $[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$ in degrading the CR and MB with maximum absorbance at 498 nm and 663 nm, respectively, was investigated. UV-Vis absorption spectroscopy was used for monitoring the reduction procedure (Figures 11 and 12). The degradation of CR and MB was completed without any delay in the existence of $[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$. Table 3 represents the degradation of MB and CR (Scheme 5).

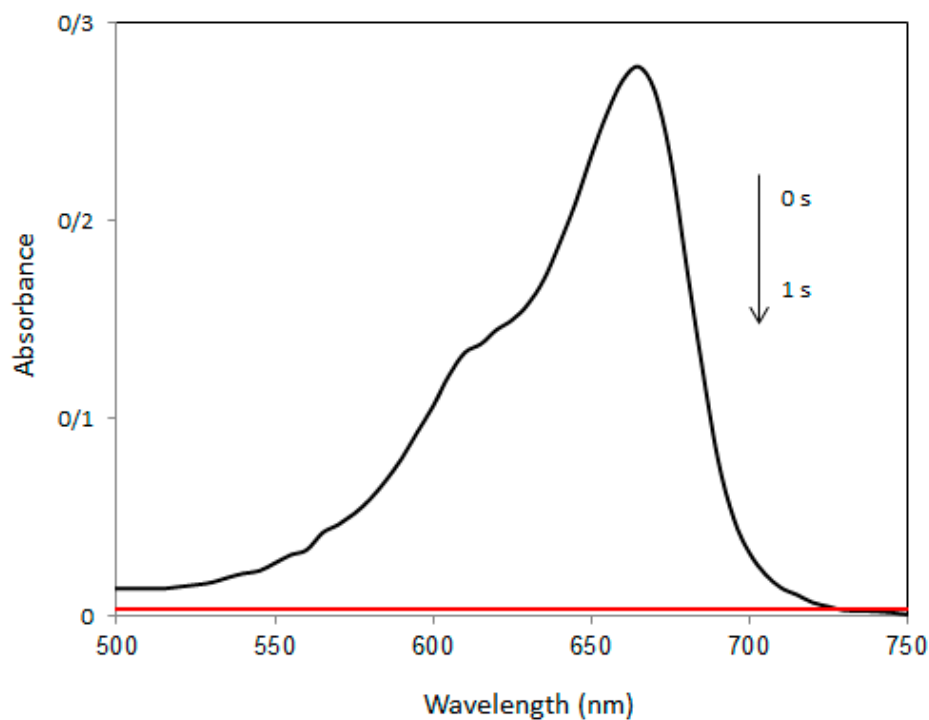


Figure 11. The UV-visible spectrum of the methylene blue degraded by NaBH_4 in $[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$ at different time of reaction.

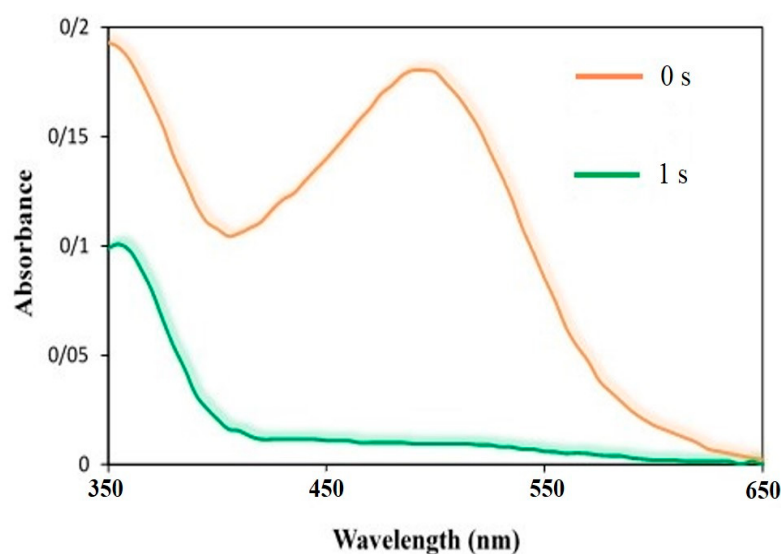
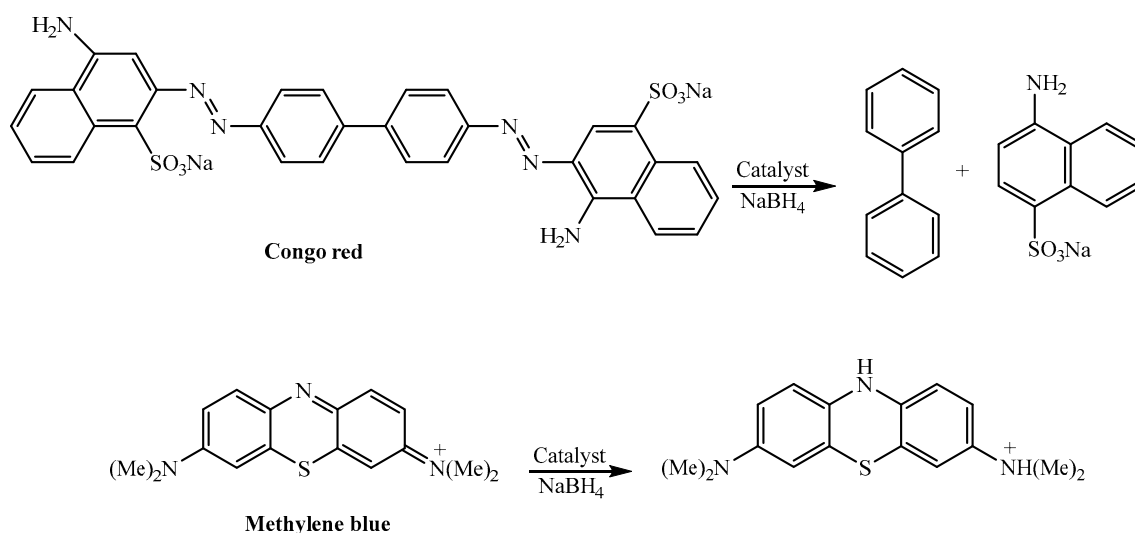


Figure 12. The UV-visible spectrum of the degraded Congo Red by NaBH_4 in $[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$.

Table 3. Optimizing conditions for the degradation of methylene blue and Congo Red applying $[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$.

Entry	Dye	Catalyst (mg)	NaBH_4 (M)	Time
1	MB	$[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$ (7.0)	5.3×10^{-3}	Immediately
2	MB	$[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$ (5.0)	5.3×10^{-3}	3 s
3	MB	$[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$ (3.0)	5.3×10^{-3}	12 s
4	CR	$[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$ (7.0)	5.3×10^{-3}	Immediately
5	CR	$[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$ (5.0)	5.3×10^{-3}	6 s
6	CR	$[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$ (3.0)	5.3×10^{-3}	15 s



Scheme 5. The schematic degradation of methylene blue and Congo Red utilizing magnetic nano-catalyst.

4. Catalyst Reusability

Synthesizing recyclable nano-catalysts with high catalytic performance is an essential issue from green and environmental viewpoints. The reusability of the magnetic nano complex $[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$ in the reduction reaction of 4-NP was investigated in this work. The $[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$ nano complex catalyzed the 4-NP reduction numerous times, as shown in Figure 13. After the reduction reaction was completed, an external magnetic

field was employed to separate the catalyst, which was then reused without significant loss of catalytic activity in subsequent runs. The slow deactivation of $[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$ attests to the catalyst's great consistency under reaction conditions. The catalyst was easily separated and retained 83% of its efficiency after five cycles without considerable loss of activity and stability (Table 4, Figure 14).



Figure 13. Magnetic removal and recoverability of nanocatalyst for 4-NP reduction at room temperature.

Table 4. The reusability of $[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$ and reaction time for the reduction of 4-NP to 4-AP.

Entry	Cycle	NaBH_4 (Equivalents)	Catalyst (mg)	Time
1	Fresh	100	$[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$ (7.0)	114 s
2	1st recycle	100	$[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$ (7.0)	118 s
3	2nd recycle	100	$[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$ (7.0)	121 s
4	3rd recycle	100	$[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$ (7.0)	125 s
5	4th recycle	100	$[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$ (7.0)	131 s
6	5th recycle	100	$[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$ (7.0)	137 s

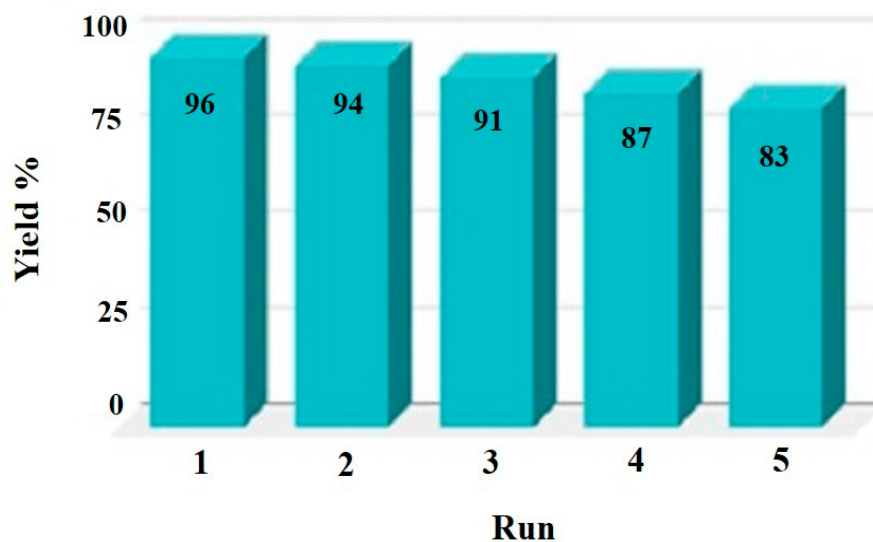


Figure 14. Diagram of magnetic nanocatalyst after applying five times in the reaction.

5. Comparison of Some Catalysts

In this work, we used $[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$ as a magnetic catalyst to degrade dye pollutants such as Congo Red and methylene blue and reduction of 4-nitrophenol and heavy metals such as chromium(VI). Remarkably, the reaction time with our catalyst is better than other works (Table 5). As a result, the reason for this difference in reaction time can be attributed to the presence of copper in our nanocatalyst structure.

Table 5. Comparison of some catalysts effects with $[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$ for the reduction of 4-NP to 4-AP.

Entry	Catalyst	Application	Reaction Time	Ref
1	rGO-BP-Pd	Reduction of 4-NP	15 min	[58]
2	Pd NPs doped chitosan	Reduction of 4-NP	35 min	[59]
3	N-C/Cu/N-C	Reduction of 4-NP	12 min	[60]
4	Ag–Cu bimetallic	Reduction of 4-NP	30 min	[61]
5	p(AAc-co-AAm)-Cu	Reduction of 4-NP	12 min	[62]
6	$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}$	Reduction of 4-NP	114 s	This work

6. Conclusions

The goal of this study is to develop a simple and straightforward method for immobilizing the Cu complex on the surface of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ as a magnetically recoverable catalyst for the reduction of 4-NP, Cr(VI), MB, and CR in water. SEM, FT-IR, XRD, VSM, TG-DTA, and EDS were used to characterize the $[\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-L-Cu(II)}]$. We discovered that this catalyst is effective in reduction/degradation of environmental pollutants in an aqueous medium, and that this technique has several advantages, including high efficiency, reduced environmental risks, and a simple working procedure. The results show that the catalyst was easily separated and retained 83% of its efficiency after five cycles without considerable loss of activity and stability.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/cryst12060862/s1>. Scheme S1: Enol-ketone tautomerization of Schiff base, L ligand. Scheme S2: The coordination method of the L Schiff base ligand. Table S1: Some physical characteristics of L ligand. Figure S1: FT-IR spectrum of L ligand.

Author Contributions: J.D., Conducted the experiments, writing—original draft preparation; M.K., writing—original draft preparation; B.M., writing—review and editing; Y.H., supervision, writing—review and editing and S.W.J., project administration and editing. All authors have read and agreed to the published version of the manuscript.

Funding: This work was funded by grant NRF-2019R1A5A8080290 of the National Research Foundation of Korea.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors acknowledge the help of Sayyed Jamaledin Asadabadi University and Qom University.

Conflicts of Interest: The authors declare no conflict of interest.

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