Reduction of toxic organic dyes in aqueous media using N-heterocyclic copper(II) complex immobilized on the beta-cyclodextrin-modified Fe3O4 nanoparticles as a magnetically recyclable catalyst

Zohreh Mehri Lighvan (z.mehri@ippi.ac.ir)
Iran Polymer and Petrochemical Institute

Hossein Ali Khonakdar
Iran Polymer and Petrochemical Institute

Bahar Khodadadi
University of Qom

Mina Rafie
Isfahan University of Technology

Azar Ramezanpour
Isfahan University of Technology

Abolfazl Heydari
Polymer Institute of the Slovak Academy of Sciences

Sara Pirani
Iran Polymer and Petrochemical Institute

ali akbari
Urmia University of Medical Sciences

Research Article

Keywords:

Posted Date: November 22nd, 2022

DOI: https://doi.org/10.21203/rs.3.rs-2277506/v1

License: This work is licensed under a Creative Commons Attribution 4.0 International License.
Read Full License
Abstract

Water supplies have been jeopardized owing to increased population and industrial activity. Azo dyes are regarded as hazardous substances, e.g. p-nitrophenol, causing cancer in animals as well as redox-related toxicity in diverse tissues. In this regard, adsorption process alone is not sufficient to treat wastewaters including extra types of pollution merely in a single step. With the purpose of declining azo-based contaminations in nontoxic species of wastewater, this paper proposed a novel functionalized iron oxide nanoadsorbent (Fe₃O₄@CM-β-CDP@Tet-Cu(II)), synthesized by combining the benefits of magnetic nanoparticles, carboxymethyl-β-cyclodextrin, and N-heterocyclic copper complex. Different techniques were employed to distinguish catalyst morphology and structure. Moreover, at room temperature, with moderate and safe reducing agents (NaBH₄), the nanocatalyst was exploited with the purpose of diminishing organic dyes such as p-nitrophenol, Eosin Y, Rhodamine B, Congo red, and Methyl orange. A simple and readily available method was employed to record such reduction: UV-vis spectroscopy. Results revealed considerable catalytic activity of Fe₃O₄@CM-β-CDP@Tet-Cu(II) besides remarkable reduction rate in the course of limited reaction time, in particular for Methyl orange dye. It is noteworthy that the catalytic activity of the nanocomposite did not suffer any notable losses despite being recovered and re-used five times. Through the use of an external magnet, such nanocomposites can be simply isolated from water environments and thereafter be exploited for organic catalytic reduction and wastewater treatment on a large scale.

1. Introduction

Nowadays, water contamination has been regarded as one of the most severe dangers to aquatic ecosystems as a result of rapid industrialization. The existence of all living organisms heavily depends on the availability of clean water. Despite this, synthetic dyes, known as one of the most severe pollutant sources of water resources, have been found to be discharged indiscriminately from various industries, including textiles, cosmetics, paper and pulping, leathering, printing, painting, dyeing, dye manufacturing, to name but a few, causing severe environmental problems[1]. Treatment of wastewater has been proposed through disparate techniques including, adsorption, membrane filtration, chemical precipitation, photocatalytic degradation, biodegradation, coagulation and flotation, membrane process, electrolytic chemical treatment, membrane technology, catalytic ozonation [2–4]. Notwithstanding this fact, there are some common downsides to the strategies listed above, such as the ineffectiveness of biodegradation for treating industrial chemicals owing to biomass poisoning. Thermal wet air oxidation of effluents with greater than 100 g L⁻¹ chemical oxygen demand engenders considerable quantities of harmful byproducts including dioxins and furans. [5]. Aiming at eliminating/reducing harmful chemical pollutants, current effective essential techniques such as reduction/degradation procedures in industrial and synthetic chemistry, must be developed. (e.g. nitroarenes, azo dyes and heavy metals) [6–8].

There has been a recent boom in the exploitation of metal complexes in various fields including biotechnology, materials science, and chemistry. [9]. Coordination compounds are utilized primarily in
homogeneous catalysis with the purpose of producing organic compounds. However, when it comes to homogeneous catalysis, separating and reusing the reactants from the reaction mixtures is the major problem. To overcome the given issue, preparation of heterogeneous catalysts must be performed through suitable supports such as natrolite zeolite\[10\], sodium borosilicate\[11\], titanium oxide \[12\], perlite \[13\] and metal oxide (MO) nanoparticles \[14–17\].

MO nanostructures are particularly appealing due to their potential properties\[18, 19\]. In this line of thought, superparamagnetic iron oxide nanoparticles (Fe$_3$O$_4$ NPs) received particular attention out of their easy magnetic separation behavior, biocompatibility, small size, being cost-effective, and abundance of surface reactive groups \[15\]. Nonetheless, the loss in effective surface area induced by their inclination to aggregate in aqueous solutions owing to high surface free energy, simple oxidation, and strong magnetic dipole-dipole interaction amongst nanoparticles limits their uses\[20, 21\]. Improving the dispersibility and stability of Fe$_3$O$_4$ NPs, diverse modifications were examined by the addition of different compounds \[22, 23\]. Thus far, a core-shell structure has been designed to facilitate the synthesis of functionalized composites\[24\]. Concerning such structures, the nanoparticles are segregated through an outer shell, hindering their migration and coalescence in the course of catalytic processes. \[15\]. Hence, several studies have been undertaken aiming at describing the functional shells such as cyclodextrins \[25\], silanes \[26\], metal organic framework \[27\], and covalent organic framework \[28\].

Biopolymers currently perform as a surface capping agent in the case of MO nanoparticles encapsulation or embedment\[29\]. β-cyclodextrin (β-CD) has considerable promise in water treatment as a result of its ability to compound with disparate organic and inorganic contaminants encompassing heavy metals, pesticides, organic dyes, and other pollutants.\[30–32\]. Moreover, β-CD derived from the enzymatic starch degradation is a torus-shaped cyclic oligosaccharide along with a hydrophilic outside and hydrophobic inside cavity\[33\]. By interacting with organic molecules, particularly aromatic compounds, this structure is known to form inclusion complexes in both solution and solid state \[34\] \[35\]. In contrast, the alteration of Fe$_3$O$_4$ nanoparticles with β-CD results in a product with molecular recognition and enrichment capabilities \[36\]. In addition, natural polymers are commonly cited as excellent adsorbents for the elimination or recovery of perilous dyes and heavy metals.. Attarchi et al. (2013) developed and evaluated the Ag/TiO$_2$/β-CD nanocomposite for the purpose of photocatalytic activity in degradation of methylene blue dye \[37\]. Ramavandi et al. created CNT/β-CD/MnFe$_2$O$_4$ magnetic nanocomposite in order to eliminate tetracycline antibiotics from aqueous solutions, meanwhile investigating its adsorption performance as well \[38\]. Yang et al. also reported the self-assembly of a bioinspired catecholic cyclodextrin TiO2 hetero-supramolecule in the case of a high adsorption capacity and effective visible-light photoactivity. \[39\]. Badruddoza et al. scrutinized Fe$_3$O$_4$/CDP nanocomposites aiming at the selective disposal of heavy metals from industrial effluent. \[40\]. As for the bifunctional adsorbent, Furtermore et al. made ethylenediaminetetraacetic acid β-CD for simultaneous metal and dyes adsorption \[41\]. Additionally, with the goal of eliminating malachite green (MG) from aqueous solution, Chen et al. created a unique β-CD-graphene oxide nanocomposites (Fe$_3$O$_4$/β-CD/GO)\[42\]. Fe/HT-DS/β-CD nanocomposites were developed in a research by Carlos Roberto Bellato et al. to eliminate phenol (PHE), p-nitrophenol (p-
NP), and p-cresol (PCS) from pulp and paper industry effluent and river water samples [43]. According to Pan et al., they discovered that β-cyclodextrin-polyethyleneimine bi-functionalized magnetic (Fe$_3$O$_4$-PEI/β-CD) hybrid composite could be employed to remediate wastewater contaminated with methyl orange (MO) and lead (II) ions. [44].

The goal of this study was to propose a new iron oxide nano-adsorbent composed of Fe$_3$O$_4$ nanoparticles as a core, along with the CM-β-CDP shell functionalized with Cu(II) 5-Amino-1H-tetrazole monohydrate complex as a ligand on the surface of the Fe$_3$O$_4$@CM-β-CDP nanoparticles. Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), and vibrating sample magnetometer were all employed to characterize the structural, morphological, and nano-iron oxide properties of the nano-adsorbent (VSM). Besides this, the reduction ability of the novel nano-adsorbent, [Fe$_3$O$_4$@CM-β-CDP@Tet-Cu(II)], under an aqueous environment was scrutinized against different organic dyes as the target pollutants, including Rhodamine B (RhB), Eosin Y (EY), p-nitrophenol (p-NP), Methyl orange (MO), and Congo red (CR).

2. Materials And Methods

2.1. General

Materials were exploited once provided from Merck Company, which included iron chloride hexahydrate (FeCl$_3$·6H$_2$O, 99.0%), iron (II) chloride tetrahydrate (FeCl$_2$·4H$_2$O 98.0%), sodium hydroxide (NaOH, 97.0%), sodium borohydride (NaBH$_4$, 98%), monochloroacetic acid (99.0%), β-cyclodextrin (β-CD, 97.0%), 5-Amino-1H-tetrazole monohydrate (99.0%), copper(II) chloride (CuCl$_2$, 99.0%), epichlorohydrin (99.0%), ethanol (99.7%), and acetone (99.5%). It should be mentioned that the water utilized was ultrapure water derived from a Milli-Q equipment (Millipore, Bedford, MA. USA).

Recording the Fourier transform infrared spectra was carried out by means of potassium bromide tablets with the FT-IR spectrophotometer (JASCO 680 PLUS) within the range of 400–4000 cm$^{-1}$. Also, UV-vis spectra on a double-beam spectrophotometer was used to investigate the reduction ability of nanocomposite for organic dyes (Shimadzu, U-2900). Considering bright field imaging at 120 kV, TEM microscopy (microscope Tecnai G2 Spirit Twin 12, FEI, Czech Republic) was hired to determine both the size and form of the Fe$_3$O$_4$@CM-β-CDP@Tet-Cu nanoparticles. Furthermore, energy dispersive spectroscopy was hired to confirm the elemental composition of the nanoparticles (EDX; detector EDAX, USA was attached to the TEM microscope described above). In addition to the nanocomposite characterization, high-resolution FE-SEM microscopy (microscope MIRA, TESCAN, Czech Republic) was used with the secondary electron imaging at 15 kV. XRD measurement was carried out by means of a Philips powder diffractometer type PW 1373 goniometer (Cu K$_\alpha$ = 1.5406 Å), with a scanning rate of 2° min$^{-1}$ and the range of 10 to 90° for 2θ. Vibrating sample magnetometer (VSM) was measured by a SQUID magnetometer 20 at 298 K (Quantum Design MPMS XL). Thermal analysis (TGA and DTG) was
performed using STA 1500 Rheometric Scientific (England) along with the air flow rate and ramping ratio of 120 mL·min⁻¹ and 2 °C·min⁻¹, respectively.

2.2. Synthesis of magnetic nanocomposite [Fe₃O₄@CM-β-CDP@Tet-Cu (II)]

2.2.1. Preparation of Fe₃O₄ nanoparticles

In accordance with the existing literature review, the microwave irradiation (MW) approach was used for synthesizing Fe₃O₄ nanoparticles [15]. In brief, 1.2 g of FeCl₂·4H₂O and 2.7 g of FeCl₃·6H₂O were dissolved in 50 mL of water under argon flow. Under magnetic stirring, thereafter, 50 mL of 25 wt % NaOH solution was added to adjust the solution pH to 9. 30 minutes of stirring were then performed under an argon atmosphere. The resultant black slurry mixture was thereafter irradiated with 2.45 GHz MW for 30 minutes in a water bath. A vacuum oven at 70°C was utilized to dry Fe₃O₄ nanoparticles after they had been separated, washed five times with ethanol and water, and then dried with water.

2.2.2. Preparation of carboxymethyl modified β-CD polymer (CM-β-CDP)

In this investigation, the CM-β-CD polymer was provided in accordance with the technique outlined in the literature[45]. To do this, 2.5 g of β-CD was firstly dissolved in 25 ml of 10 wt% of NaOH solution and followed by a 30-minunute stirring at room temperature. Following that, epichlorohydrin (10 mL) was added and the resultant solution was again stirred for 8 h at 30° C. Epichlorohydrin (5 mL) was then added to the mixture, and the reaction was allowed to run for 24 hours at room temperature. As a result of decreasing the solvent and adding an excessive amount of cold ethanol to the reaction mixture, a gummy precipitate was engendered. The resultant material was reduced to fine powder out of crushing multiple times in a mortar with ethanol and drying under vacuum for 24 hours. Then, 50 mL of 5% NaOH was used to dissolve 2 g of the obtained polymer and 2 g of monochloroacetic acid was added into the reaction mixture, followed by rapid stirring at ambient temperature for 24 h. The resultant solution was neutralized with concentrated HCl and cooled to 4° C. The gum product was then crushed several times with ethanol in a mortar to provide a fine powder. The product was separated and dried in vacuum oven at 50°C for 8 h. FT-IR (KBr), ν (cm⁻¹): 3140–3670 (-OH), 2928 (-CH), 1709 (C = O), 970–1200 (C–C–C, C–O–C) (see Fig. 1).

2.2.3. Preparation of core-shell nanocomposite (Fe₃O₄@CM-β-CDP)

Having dissolved 1.1 g of Fe₃O₄ nanoparticles and 1.5 g of CM-β-CDP in 40 mL deionized water and heated the solution to 90°C, 5 mL of NH₄OH (25%) was added to the solution, which was then stirred continuously subjected to nitrogen atmosphere for one hour.. The resultant nanoparticles were washed
five to six times with water in order to eliminate the unreacted raw materials before drying in a vacuum oven at 40°C.

2.2.4. Functionalization of Fe$_3$O$_4$@CM-β-CDP by (3-chloropropyl) trimethoxysilane (Fe$_3$O$_4$ @CM-β-CDP@SiO(CH$_2$)$_3$-Cl)

The 1 g dissolved Fe$_3$O$_4$@CM-β-CDP in 80 mL of toluene was irradiated for 15 minutes under ultrasonic bath at room temperature. Following that, 3 mL of (3-chloropropyl) trimethoxysilane was gently added to the reaction mixture, which was then stirred for 24 hours under reflux conditions. In the end, the catalyst was extracted using an external permanent magnet, washed three times with distilled water and toluene, and dried in a vacuum oven at 80°C for 6 h. Surface modification was accomplished through the nucleophilic substitution reaction between the amino tetrazole group and the leaving group in Fe$_3$O$_4$@β-CDP-SiO(CH$_2$)$_3$-Cl. For this purpose, 2 g of the preceding step’s product was combined with 50 mL of DMF, 1.195 g (5 mmol) of 5-amino-1-tetrazole monohydrate and 0.691 g (5 mmol) of K$_2$CO$_3$, and then stirred under reflux conditions for 24 hours. Eventually, the catalyst was magnetically extracted from the reaction mixture, washed with ethanol, and dried under vacuum overnight.

2.2.5. Preparation of [Fe$_3$O$_4$@CM-β-CDP@Tet-Cu (II)]

As for the final stage, 1 g of previously synthesized nanocomposite (Fe$_3$O$_4$@CM-β-CDP-SiO (CH$_2$)$_3$-aminotet), 0.4 g of CuCl$_2$ and 50 mL of methanol as solvent were refluxed for 24 h. The resultant precipitate was thereafter collected from the reaction mixture using a magnet at the conclusion of the reaction, washed with ethanol, and dried in an oven at 80°C providing a cupper magnetic complex.

2. 3. Catalytic Activity Of [feo@cm-β-cdp@tet-cu(II)]

2.3.1. Catalytic reduction of p-nitrophenol (p-NP)

In order to validate the catalytic activity of the produced nanoparticles, the liquid-phase reduction of p-NP to p-aminophenol (p-AP) using NaBH$_4$ was investigated. Concisely, 5 mg of the Fe$_3$O$_4$@CM-β-CDP@Tet-Cu complex was added to 25 mL of a p-NP solution (2.5 mM), which was thereafter stirred for 1 min at room temperature. Following that, 25 mL of freshly provided NaBH$_4$ aqueous solution (25 mL, 250 mM) was introduced for the reaction commence. The shift in color from yellow to colorless, which was visible with the naked eye, was tracked by collecting UV-vis spectra in the 200–500 nm region. By the end of each cycle, the catalyst was extracted by magnet, washed, dried and reused in another cycle to investigate catalyst recyclability.

2.3.2. Catalytic reduction of organic dyes (EY, RhB, CR, MO)
Evaluating dye degradation ability of the nanocatalyst, 12 mg of Fe₃O₄@CM-β-CDP@Tet-Cu (II) was introduced to 25 mL of diverse azo dyes including RhB (200 mM), CR (200 mM), MO (100 mM), and EY (100 mM) at pH = 6.5). The reaction mixture was next stirred at room temperature (400 rpm) after the addition of freshly produced NaBH₄ solution (25 mL, 5.3 mM). The variation in the absorption peak at the maximum wavelength of each dye revealed dye degradation in the course of the reduction process with NaBH₄ at the presence of magnetic catalyst. The catalyst was extracted from the reaction mixture using a magnet at the conclusion of the reaction, washed with distilled water and ethanol, and ultimately dried for the next run of the reaction.

3. Results And Discussion

The production procedures for the Fe₃O₄@CM-β-CDP@Tet-Cu nanocatalyst are depicted in Scheme 1. As can be seen, the surface of Fe₃O₄ nanoparticles was functionalized by β-CD polymer, which is a natural polymer with β-CD cavities. The surface of nanoparticle was then modified via (3-chloropropyl) trimethoxysilane. Finally, nucleophilic substitution between (3-chloropropyl) trimethoxysilane and 5-amino-1-tetrazole monohydrate led to decorating the nanoparticle surface with a suitable ligand for binding of copper ions.

3.1. Characterization of Fe₃O₄@CM-β-CDP@Tet-Cu(II)

FT-IR spectroscopy was employed in this study to investigate the chemical structure of generated materials. The FT-Figure 1 illustrates the IR spectra of CM-β-CDP, Fe₃O₄@CM-β-CDP, Fe₃O₄@CM-β-CDP@SiO(CH₂)₃-Cl, and Fe₃O₄@CM-β-CDP@Tet-Cu. The bands at 1031 and 1155 cm⁻¹ in the CM—CDP spectra correspond to C-O-C asymmetric glycosidic vibrations and vibration of C-C/C-O bonds, respectively. The C = O stretching vibration observed at 1720 cm⁻¹ testifies the incorporation of carboxymethyl groups into the β-CDP structure [40]. O-H stretching and C-H asymmetric vibrations can be seen by the wide bands at 3500 – 3300 and 2925 cm⁻¹, respectively. The distinctive bands of Fe₃O₄ nanoparticles found between 500 and 750 cm⁻¹ can be ascribed to Fe-O-Fe vibrations, indicating the formation of Fe₃O₄ nanoparticles[46]. The observed bands at 1045 and 833 cm⁻¹ following the treatment with (3-chloropropyl) trimethoxysilane could be attributed to the asymmetric and symmetric stretching of Si-O-Si, respectively, supporting the salinization reaction occurred on the surface of nanoparticles. Note that the stretching vibration of N = N bonds in the structure of ligands was observed at 1421 cm⁻¹. Based on all of the distinctive bands, it is possible to infer that the Fe₃O₄@CM-β-CDP-Tet-Cu (II) nanocomposite was effectively synthesized.

3.2. Structural and Morphological Study

As provided in Fig. 2, the XRD pattern of Fe₃O₄@CM-β-CDP@Tet-Cu(II) was scrutinized with the purpose of assessing any phase formation and crystallization. In addition to the given Fig. 2, peaks at 2θ values
of 11.60, 16.65, 28.35, 35.68, 37.62, 63.13, 66.34, 73.72 and 37.62 are pertinent to (110), (111), (220), (311), (222), (400), (422), (511), (440), (620), (533) crystal planes of Fe$_3$O$_4$ nanoparticles, respectively ((JCPDS 19–0629) [47]. It is worth noting that these peaks are identical to the Fe3O4 cubic spinel structure. Through the Debye-Scherrer equation, the observed wide peaks revealed the crystalline nature of the material, which was determined to be 68.48%, along with the average crystallite size of 18 nm. As compared to bulk Fe$_3$O$_4$ nanoparticles, Fe$_3$O$_4$@CM-β-CDP@Tet-Cu(II) nanoparticles had a fairly smaller cell parameter (0.842 nm). The observed peaks at 2θ values of 40.57, 50.21 and 74.60 can be pertinent to (111), (200) and (220) crystal planes in Cu cubic structure, revealing a well-matched agreement with the standard Cu (JCPDS 71-4610) [48]. The XRD measurements approved that the Fe$_3$O$_4$@CM-β-CDP-Tet-Cu(II) nanocomposite was successfully prepared.

Characterization of nanoparticle morphology, distribution, and also the shape was carried out by means of FE-SEM and TEM images. Based on the FE-SEM images, one could notice the homogeneous distribution of Fe$_3$O$_4$ nanocrystals as spherical particles (see Fig. 3a). Furthermore, the Fe$_3$O$_4$@CM-β-CDP@Tet-Cu(II) core-shell TEM images denoted a reasonably broad size range with an average diameter of around 30 nm (see Fig. 3B). Aside from that, compared to the dark inner Fe3O4 nucleus, these images depicted a continuous layer with a better brightness. As a result, it can be inferred that Fe$_3$O$_4$@CM-β-CDP@Tet-Cu(II) was surrounded by a typical core-shell structure.

An EDX analysis (II) was performed on Fe$_3$O$_4$@CM-β-CDP@Tet-Cu(II), consequently approving the presence of C, N, Si, O, Cl, Fe and Cu elements in the structure (Figure. 4). The sources of C and N were originated from β-CDP and tetrazole ligand on the surface, on the other hand, O and Fe elements were basically stemmed from Fe$_3$O$_4$ nanoparticles and β-CDP. Furthermore, the examination of the Si peak ascertained the effective functionalization using the (3-chloropropyl) trimethoxysilane reagent. Also, the existence of Cu in the core-shell structure was proven by the appearance of cupper related peaks in the spectrum. Based upon the resultant weight percentages from EDX analysis, the Fe$_3$O$_4$@CM-β-CDP@Tet-Cu(II) structure contained approximately 5.24% (1.75% atomic) of Cu weight.

According to Fe, Cu, C, N, O, and Si EDX mapping in the Fe$_3$O$_4$@CM-β-CDP@Tet-Cu(II) nanocomposite one could notice the distribution of Fe$_3$O$_4$ microspheres as the core of structure, highlighting the functionalization by tetrazol ligand and β-CDP. Additionally, the uniform distribution of Cu element in the structure can be inferred from the elemental mapping of Fe$_3$O$_4$@CM-β-CDP@Tet-Cu(II)(Fig. 5).

### 3.3. Magnetic Properties

Aiming at evaluating the magnetic property from the hysteresis loops at ambient temperature, the VSM technique was employed. Figure 6 indicates the magnetic hysteresis loop (M-H loop) of Fe$_3$O$_4$@CM-β-CDP@Tet-Cu(II) core-shell microspheres at 25°C along with the illustration of S-like for nanocomposite cases [49]. The saturation magnetization value ($M_s$), coercivity ($H_c$) and remnant magnetization ($M_r$) of nanocomposites were determined to be 16.17 emu/g, 135.90 Oe and 3.65 emu/g, respectively. Due to the
modification of iron oxide nanoparticles with CM-β-CDP shell and tetrazole ligand, the nano complex had a lower magnetic saturation than bulk Fe3O4 (~ 92 emu g⁻¹)[50], [51]. Additionally stated, the reduction in magnetic susceptibility with particle size can be ascribed to spin disorder at the particle surface generated by surface inhomogeneities and truncation of the crystalline lattice [49, 52, 53]. Therefore, the inability of magnetic molecules on the surface to complete coordination increases surface spin disorientation. [54]. Despite this fact, in the case of an external magnet, the fast aggregation of the particles from their homogenous suspension and their rapid redispersion may be accompanied with shaking once the magnetic field is removed. These findings add to the evidence supporting the nanocatalyst's strong magnetic responsivity and re-dispersibility, which is an important factor in the case of industrial applications.

3.4. Thermal Properties

Providing additional evidences for surface and thermal stability alteration of nanocatalyst, thermogravimetric analysis (TGA) and differential thermal analysis (DTG) were performed under air atmosphere at a heating rate of 2 °C·min⁻¹ in a temperature range of 100–850 °C (Fig. 7). The TGA and DTG curves of Fe₃O₄@CM-β-CDP@Tet-Cu(II) depicts a multistep endothermic thermal decomposition beginning with the removal of adsorbed water and solvent temperatures ranging from 150 to 245 °C, causing a weight loss of 6.45%. This is in contrast to those weight losses in the other processes at the temperatures ranging within 250–850 °C, which are attributable to organic components of the structure such as tetrazol ligand, (3-chloropropyl) trimethoxysilane, β-CDP, and carboxymethyl groups, approving the surface functionalization. Residual magnetic weight was determined about 60% for Fe₃O₄@CM-β-CDP@Tet-Cu(II) nanocatalyst. These findings reveal that the Fe₃O₄@CM-β-CDP@Tet-Cu(II) catalyst has high thermal stability and can potentially catalyze the majority of organic processes.

3.5. Catalytic properties of Fe₃O₄@CM-β-CDP@Tet-Cu(II)

Regarding the merits of β-CD, including special structure, biocompatibility, and cost-effectiveness, it has been an appealing choice for many industrial applications, ranging from medicine, supramolecular chemistry to water treatment since late 1980s [55]. Both factors of the CD molecules’ specific structures and their hydrophobic cavity facilitate the encapsulation of small molecules and besides, the creation of inclusion complexes are governed by host-guest interactions. [56]. It is worth mentioning that when exposed to aquatic circumstances, water molecules bound by weak forces occupying the hydrophobic CD cavity, resulting in the formation of host (CD)-guest complexes by supplanting water molecules with hydrophobic molecules serving as guests [57].

3.5.1. Catalytic reduction of p-nitrophenol (p-NP)

Assessing the catalytic activity of the resultant Fe₃O₄@CM-β-CDP@Tet-Cu(II) nanocatalyst, the reduction process of p-NP to corresponding amine (p-AP) was examined in the presence of NaBH₄ as a selective
and cost-effective reducing agent under moderate reaction conditions [58]. Furthermore, water is not only an ecologically permissible solvent but also supplies proton, stabilizes charged species within the reduction process of p-NP, and boosts the reaction rate[59].

The UV-Vis spectra of an aqueous p-NP solution reveal that the absorption peak at 317 nm moves to 400 nm following the addition of NaBH₄. Furthermore, the color of the reaction mixtures turns from yellow to dark yellow, confirming the formation of p-nitrophenolate species. Note that the conversion of p-NP to p-AP was moderate in the presence of NaBH₄, with no discernible progress observed in the absence of the nanocatalyst (Table 1, entry 1). Needless to say, the decline of p-NP ($E_0 = -0.76$ V) by using NaBH₄ ($E_0 = -1.33$ V) is thermodynamically conceivable, however, it is kinetically limited in the lack of a sufficient catalyst in the aqueous NaBH₄ solution [60]. Such conclusion also reveals that the aqueous NaBH₄ solution was insufficient for the occurrence of the reduction process. Following the addition of the catalyst, the reduction progress was measured through tracking the changes at 400 nm and the appearance of a new peak at 298 nm, which is followed by the shift in solution's yellow color to colorless(Figure. 7 (a)). Such color alteration was noticed in a short period of time (3 min), pinpointing the creation of p-AP product. With the aim of investigating the influences of various nanocomposites and NaBH₄ contents on catalytic reduction of p-NP, the optimum results were achieved by the use of 5 mg nanocomposite and 100 equivalents of NaBH₄ (Table 1, entry 4). The entries 1 and 3 (Table 1) shed light on the occurrence or accomplishment of no reaction in the absence of the nanocomposite or NaBH₄. The catalytic reduction of p-NP was accomplished in two steps, as one could see in the reaction mechanism (Fig. 7B). First, diffusion of BH$_4^-$ and p-NP from aqueous solution to the surface of catalyst via host – guest character of β-CD [56], and second, the catalytic reduction process of p-NP to p-AP is an electron transfer process and the nanocatalyst Fe$_3$O$_4$@CM-β-CDP@Tet-Cu(II) serves as an intermediate for transferring electron reagent via several steps including p-NP adsorption, production $[\text{BO}_2]^-$ and H$_2$ species, hydride transfer through catalyst and reduction and desorption amine products [61]. Owing to the wide surface area of the nanocomposite, the adsorption of p-NP anions was boosted, leading to greater catalytic activity.
Table 1
Optimization conditions for the reduction of the p-NP using Fe$_3$O$_4$@CM-β-CDP@Tet-Cu(II) at ambient temperature.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Nanocatalyst (mg)</th>
<th>NaBH$_4$ (equivalents)</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NA</td>
<td>100</td>
<td>180$^a$</td>
</tr>
<tr>
<td>2</td>
<td>Fe$_3$O$_4$ (12)</td>
<td>100</td>
<td>110$^b$</td>
</tr>
<tr>
<td>3</td>
<td>[Fe$_3$O$_4$@CM-β-CDP@Tet-Cu] (12)</td>
<td>0.0</td>
<td>260$^b$</td>
</tr>
<tr>
<td>4</td>
<td>[Fe$_3$O$_4$@CM-β-CDP@Tet-Cu] (12)</td>
<td>100</td>
<td>3</td>
</tr>
<tr>
<td>5</td>
<td>[Fe$_3$O$_4$@CM-β-CDP@Tet-Cu] (8)</td>
<td>100</td>
<td>9</td>
</tr>
<tr>
<td>6</td>
<td>[Fe$_3$O$_4$@CM-β-CDP@Tet-Cu] (4)</td>
<td>100</td>
<td>20</td>
</tr>
<tr>
<td>7</td>
<td>[Fe$_3$O$_4$@CM-β-CDP@Tet-Cu] (12)</td>
<td>80</td>
<td>8</td>
</tr>
<tr>
<td>8</td>
<td>[Fe$_3$O$_4$@CM-β-CDP@Tet-Cu] (12)</td>
<td>70</td>
<td>19</td>
</tr>
<tr>
<td>9</td>
<td>[Fe$_3$O$_4$@CM-β-CDP@Tet-Cu] (12)</td>
<td>50</td>
<td>32</td>
</tr>
</tbody>
</table>

3.5.2. Catalytic reduction of Rhodamine B (RhB)

Rhodamine B (RhB), regarded as one of the widespread cationic dye with dark red color, was opted as a model assessing the catalytic ability of Fe$_3$O$_4$@CM-β-CDP@Tet-Cu(II) nanocatalyst due to its broad applications in dyeing (Asraf-Snir and Gitis 2011), fluorescence correlation spectroscopy (LaRochelle et al. 2015), and health impacts [62]. With this in mind, reduction process of RhB was tracked at room temperature by recording variations in absorption intensity of peaks in the UV-Vis spectrum. Figure 9 depicts that the sharp peak within the region of 500–600 nm in the UV-Vis spectrum of RhB vanished as soon as 13 min following the addition of NaBH$_4$ and nanocatalyst.

NaBH$_4$ with Fe$_3$O$_4$@CM-β-CDP@Tet-Cu(II) catalyst has been reported to engender de-ethylation of the RhB dye by creating aromatic amines (Fig. 8B). Consequently, the new peak at 242 nm might be explained by the free amino group of aromatic amines generated from RhB degradation.

Based on the Eq. (1), the reduction rate ($\eta$) of 66.91% was determined to be 66.91%.

$$\eta = \frac{A_0 - A_t}{A_0} \times 100$$

where $A_0$ and $A_t$ are the initial absorbance and the absorbance at time $t$, respectively.
3.5.3. Catalytic reduction of Eosin Y (EY)

Eosin Y is regarded as a bromine-containing heterocyclic dye commonly employed as dye, photosensitizer on semiconductors, histological tissue sections, printing, leather and fluorescent pigment [63]. Considering the dark color and toxicity of eosin Y, the immediate release of wastewater containing this dye will cause major environmental problems [64]. The UV-Vis spectrum of EY in advance to the reduction process revealed a distinctive peak at 515 nm, which vanished after 27 minutes (Table 2, entry 13) with reduction rate of 88.15% (Fig. 10). This is clearly confirmed that the presence of nanocomposite and reducing agent is vital in catalytic reduction.

3.5.4. Catalytic reduction of Congo red (CR)

As a popular diazo dye, the CR has been widely exploited in the textile, wood, paper, and pulp industries and has also identified as a carcinogenic and teratogenic agent for humans and aquatic animals due to the inclusion of a poisonous component (benzene) in the structure. [65]. It is crucial in this line of thought to provide a simple reduction technique for CR dye. Prior to catalyst addition, the UV-Vis spectrum of CR denotes a constant strong peak at 493 nm and a weak peak at 343 nm. Notwithstanding this fact, following the catalyst addition, the absorption intensity of the mentioned peaks steadily decreased over 6.5 min (Table 2, entry 3) with a reduced rate of 92.50%. Meanwhile, a new peak emerged at 250 nm, indicating a reduction in CR at the azo site by generating amines (Fig. 11) [66]. The resultant nanocatalyst is most likely to reduce CR in line with the manner depicted in Fig. 11.

3.5.5. Catalytic reduction of methyl orange (MO)

Similarly, MO is a very common organic azo dye exploited as a pH indicator in textiles, leather, and paper manufacturing. Owing to its xenobiotic properties and complex aromatic structure, MO dye is not biodegradable and leads to a number of environmental problems [67]. A great deal of interest is therefore being placed on developing methods for MO reduction. Molecular structure of MO dye depicts a sharp peak at 463 nm, pertaining to the azo bond, and a weak peak at 282 nm in the aqueous solution. Despite the thermodynamic advantage of NaBH₄, the reduction of MO by NaBH₄ is kinetically slow, demanding a catalyst to occur. This can be seen from the intensity of peaks in the UV-Vis spectrum of MO in the presence of NaBH₄. Following the addition of the produced nanocatalyst, the peak intensities of both peaks began to progressively decrease, while the position of peak maxima at 282 nm shifted to 250 nm as the reaction progressed. (Fig. 12). A new peak at 250 nm appeared after the peak at 463 nm disappeared (Table 2, entry 18), attributed to amine reduction and free amine production. It was found that the percent of decline was around 94.83% using the UV-Vis spectrum.

The resultant nanocatalyst facilitates the electron transfer between dye and reducing agent in the catalytic reduction of organic dyes. There are many phases involved in a such reduction process, including substrate adsorption, electron transfer, dye reduction, and nontoxic product desorption.
The nanocomposite produced in this study $\text{[Fe}_3\text{O}_4@\text{CM-β-CDP@Tet-Cu]}$, compared in Table 3 to other published catalysts for reducing/degrading $\rho$-NP, RhB, CR and MO, proved to be efficient.

Table 2
Optimization conditions for the reduction of the CR, MO, RhB, and EY using $\text{[Fe}_3\text{O}_4@\text{CM-β-CDP@Tet-Cu(II)]}$ at ambient temperature

<table>
<thead>
<tr>
<th>Entry</th>
<th>Dye (M)</th>
<th>Nanocatalyst (mg)</th>
<th>NaBH$_4$ (M)</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CR (2×10$^{-5}$)</td>
<td>NA</td>
<td>5×10$^{-3}$</td>
<td>120 min$^a$</td>
</tr>
<tr>
<td>2</td>
<td>CR (2×10$^{-5}$)</td>
<td>$\text{[Fe}_3\text{O}_4@\text{CM-β-CDP@Tet-Pd]}$ (12)</td>
<td>NA</td>
<td>70 min$^b$</td>
</tr>
<tr>
<td>3</td>
<td>CR (2×10$^{-5}$)</td>
<td>$\text{[Fe}_3\text{O}_4@\text{CM-β-CDP@Tet-Pd]}$ (12)</td>
<td>5×10$^{-3}$</td>
<td>6.5 min</td>
</tr>
<tr>
<td>4</td>
<td>CR (2×10$^{-5}$)</td>
<td>$\text{[Fe}_3\text{O}_4@\text{CM-β-CDP@Tet-Pd]}$ (8)</td>
<td>5×10$^{-3}$</td>
<td>14 min</td>
</tr>
<tr>
<td>5</td>
<td>CR (2×10$^{-5}$)</td>
<td>$\text{[Fe}_3\text{O}_4@\text{CM-β-CDP@Tet-Pd]}$ (4)</td>
<td>5×10$^{-3}$</td>
<td>17 min</td>
</tr>
<tr>
<td>6</td>
<td>RhB (2×10$^{-5}$)</td>
<td>NA</td>
<td>5×10$^{-3}$</td>
<td>180 min$^a$</td>
</tr>
<tr>
<td>7</td>
<td>RhB (2×10$^{-5}$)</td>
<td>$\text{[Fe}_3\text{O}_4@\text{CM-β-CDP@Tet-Pd]}$ (12)</td>
<td>NA</td>
<td>90 min$^b$</td>
</tr>
<tr>
<td>8</td>
<td>RhB (2×10$^{-5}$)</td>
<td>$\text{[Fe}_3\text{O}_4@\text{CM-β-CDP@Tet-Pd]}$ (12)</td>
<td>5×10$^{-3}$</td>
<td>13 min</td>
</tr>
<tr>
<td>9</td>
<td>RhB (2×10$^{-5}$)</td>
<td>$\text{[Fe}_3\text{O}_4@\text{CM-β-CDP@Tet-Pd]}$ (8)</td>
<td>5×10$^{-3}$</td>
<td>29 min</td>
</tr>
<tr>
<td>10</td>
<td>RhB (2×10$^{-5}$)</td>
<td>$\text{[Fe}_3\text{O}_4@\text{CM-β-CDP@Tet-Pd]}$ (4)</td>
<td>5×10$^{-3}$</td>
<td>41 min</td>
</tr>
<tr>
<td>11</td>
<td>EY (1×10$^{-5}$)</td>
<td>NA</td>
<td>5×10$^{-3}$</td>
<td>280 min$^a$</td>
</tr>
<tr>
<td>12</td>
<td>EY (1×10$^{-5}$)</td>
<td>$\text{[Fe}_3\text{O}_4@\text{CM-β-CDP@Tet-Pd]}$ (12)</td>
<td>NA</td>
<td>200 min$^b$</td>
</tr>
<tr>
<td>13</td>
<td>EY (1×10$^{-5}$)</td>
<td>$\text{[Fe}_3\text{O}_4@\text{CM-β-CDP@Tet-Pd]}$ (12)</td>
<td>5×10$^{-3}$</td>
<td>27 min</td>
</tr>
<tr>
<td>14</td>
<td>EY (1×10$^{-5}$)</td>
<td>$\text{[Fe}_3\text{O}_4@\text{CM-β-CDP@Tet-Pd]}$ (8)</td>
<td>5×10$^{-3}$</td>
<td>41 min</td>
</tr>
<tr>
<td>15</td>
<td>EY (1×10$^{-5}$)</td>
<td>$\text{[Fe}_3\text{O}_4@\text{CM-β-CDP@Tet-Pd]}$ (4)</td>
<td>5×10$^{-3}$</td>
<td>73 min</td>
</tr>
<tr>
<td>16</td>
<td>MO (1×10$^{-5}$)</td>
<td>NA</td>
<td>5×10$^{-3}$</td>
<td>160 min$^a$</td>
</tr>
<tr>
<td>17</td>
<td>MO (1×10$^{-5}$)</td>
<td>$\text{[Fe}_3\text{O}_4@\text{CM-β-CDP@Tet-Pd]}$ (12)</td>
<td>NA</td>
<td>90 min$^b$</td>
</tr>
<tr>
<td>18</td>
<td>MO (1×10$^{-5}$)</td>
<td>$\text{[Fe}_3\text{O}_4@\text{CM-β-CDP@Tet-Pd]}$ (12)</td>
<td>5×10$^{-3}$</td>
<td>1 min</td>
</tr>
<tr>
<td>19</td>
<td>MO (1×10$^{-5}$)</td>
<td>$\text{[Fe}_3\text{O}_4@\text{CM-β-CDP@Tet-Pd]}$ (8)</td>
<td>5×10$^{-3}$</td>
<td>5 min</td>
</tr>
<tr>
<td>20</td>
<td>MO (1×10$^{-5}$)</td>
<td>$\text{[Fe}_3\text{O}_4@\text{CM-β-CDP@Tet-Pd]}$ (4)</td>
<td>5×10$^{-3}$</td>
<td>7 min</td>
</tr>
</tbody>
</table>

$^a$No reaction, $^b$Not completed, NA: not applicable
Table 3
The comparison of the findings of this work with literature data on the reduction of $p$-NP, RhB, MO, CR, and RhB.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Catalyst</th>
<th>Time</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p$-NP</td>
<td>$[\text{Fe}_3\text{O}_4@\text{CM-}\beta\text{-CDP@Tet-Cu}]$</td>
<td>3 min</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>Fe3O4@C@Pt</td>
<td>60 min</td>
<td>[68]</td>
</tr>
<tr>
<td></td>
<td>GA-Pt NPs</td>
<td>8 h</td>
<td>[69]</td>
</tr>
<tr>
<td></td>
<td>Au@PZS@CNTs</td>
<td>16 min</td>
<td>[70]</td>
</tr>
<tr>
<td></td>
<td>p(AMPS)–Co composite</td>
<td>28 min</td>
<td>[71]</td>
</tr>
<tr>
<td></td>
<td>Pd-FG</td>
<td>12 min</td>
<td>[72]</td>
</tr>
<tr>
<td>RhB</td>
<td>$[\text{Fe}_3\text{O}_4@\text{CM-}\beta\text{-CDP@Tet-Cu}]$</td>
<td>13 min</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>Fe3O4/Ag</td>
<td>15 min</td>
<td>[73]</td>
</tr>
<tr>
<td></td>
<td>Fe$_3$O$_4$@PANI@Au</td>
<td>18 min</td>
<td>[74]</td>
</tr>
<tr>
<td></td>
<td>Au-PANI nanocomposite</td>
<td>15 min</td>
<td>[75]</td>
</tr>
<tr>
<td></td>
<td>Ag/HLaNb$_2$O$_7$</td>
<td>47 min</td>
<td>[76]</td>
</tr>
<tr>
<td></td>
<td>SiNWAs-Cu</td>
<td>14 min</td>
<td>[77]</td>
</tr>
<tr>
<td>MO</td>
<td>$[\text{Fe}_3\text{O}_4@\text{CM-}\beta\text{-CDP@Tet-Cu}]$</td>
<td>1 min</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>Cu@SBA-15</td>
<td>5 min</td>
<td>[78]</td>
</tr>
<tr>
<td></td>
<td>Ag/zeolite nanocomposite</td>
<td>88 s</td>
<td>[79]</td>
</tr>
<tr>
<td></td>
<td>Cu/sodium borosilicate</td>
<td>2 min</td>
<td>[80]</td>
</tr>
<tr>
<td></td>
<td>Au@TiO$_2$</td>
<td>&gt; 12 min</td>
<td>[81]</td>
</tr>
<tr>
<td>CR</td>
<td>$[\text{Fe}_3\text{O}_4@\text{CM-}\beta\text{-CDP@Tet-Cu}]$</td>
<td>6.5 min</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>Cu@SBA-15</td>
<td>7 min</td>
<td>[78]</td>
</tr>
<tr>
<td></td>
<td>Cu/ZnO NPs</td>
<td>9 min</td>
<td>[82]</td>
</tr>
<tr>
<td></td>
<td>Copper nanocrystals</td>
<td>8 min</td>
<td>[83]</td>
</tr>
</tbody>
</table>

3.6. Recyclability of nanocatalyst

In addition to the recyclability of a nanocatalyst, green process concerns play an important role in determining a catalyst’s applicability. By rinsing the synthesized catalyst in water and ethanol, drying, and reusing it in a new cycle of reduction in the presence of NaBH$_4$ solution, the recyclability of the synthesized catalyst was investigated in reduction reactions of $p$-NP, CR, MO, and EY. Five cycles of
testing revealed only minor declines in the product yield. After the five recyclings, the TEM and FESEM images revealed no significant changes in morphological specifications of the Fe$_3$O$_4$@CM-β-CDP@Tet-Cu(II) (Fig. 13).

4. Conclusions

One of the most important challenges for environmental researchers is to develop eco-friendly and cost-effective methods for removing toxic pollutants from wastewater. The research aims to address this global issue by altering iron oxide nanoparticles with β-cyclodextrin polymer, N-heterocyclic ligands, and copper ions (II) as a low-cost transition metal. Diverse microscopic and spectroscopic approaches proved the effective fabrication of nanocatalyst. The nanocatalyst shown remarkable catalytic activity in the quick reduction process of organic dyes including p-NP, RhB, EY, CR, and MO in the presence of NaBH$_4$ at room temperature. The catalyst performance is based on enhancing the rate of electron transfer and declining the activation energy barrier. The findings highlighted the catalyst's recyclability, with the catalyst being able to be reused for five repeating cycles simply by magnetic separation of catalyst from reaction media. Importantly, the excellent catalytic activity, stability and good reusability suggest that the Fe$_3$O$_4$@CM-β-CDP@Tet-Cu(II) nanocomposite could be used as a promising alternative for the treatment of industrially discharged waste water. It should be noted that mere color shifting can often be deceiving in case of judging the success in dye removal; hence, comprehensive investigations are required to reach any meaningful consensus.

Declarations

Competing interests.

The authors declare that they have no competing interests.

Ethics approval and consent to participate.

Not applicable

Consent for publication.

Not applicable

Funding

This work was supported by the Iran National Science Foundation for their financial support (grant number 97003938), the Slovak Grant Agency VEGA under contract number 2/0140/20, and the Slovak Research and Development Agency under contract number APVV-18-0480.
Authors’ contributions.

Conceptualization: Zohreh Mehri Lighvan, Hossein Ali Khonakdar, Ali Akbari; Formal analysis and investigation: Zohreh Mehri Lighvan, Ali Akbari, Abolfazl Heydari, Mina Rafie; Writing—original draft preparation: Zohreh Mehri Lighvan, Ali Akbari, Azar Ramezanpour; Validation: Sara Pirani, Bahar Khodadadi, Writing—review and editing: Zohreh Mehri Lighvan, Ali Akbari. All authors read the final version of this manuscript and approved it for submission.

Acknowledgments

ZML acknowledge the SAIA, n. o. (Slovak Academic Information Agency) for support on the experiment provided and financial support within National Scholarship Programme of the Slovak Republic (NSP).

References