Facile fabrication of CuFe2O4 coated with Carbon Quantum Dots nanocomposite as an efficient heterogeneous catalyst toward the reduction of nitroaniline compounds for management of aquatic resources

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Facile fabrication of CuFe$_2$O$_4$ coated with Carbon Quantum Dots nanocomposite as an efficient heterogeneous catalyst toward the reduction of nitroaniline compounds for management of aquatic resources

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Abstract:

The main objective of the current study is to scrutinize the fabrication of facile carbon quantum dots (CQDs) of glucose along with CuFe$_2$O$_4$-CQD nanocomposite and its catalytic reduction towards 2-Nitroaniline (2-NA) and 4-Nitroaniline (4-NA). Considering this, glucose-CQDs and nanocomposite of CuFe$_2$O$_4$-CQD were synthesized via hydrothermal and co-precipitation methods, respectively. Afterward, the fabricated nanocomposite as a promising nanocatalyst was employed to catalyze the 2-NA and 4-NA as a model of toxic organic pollutants into the 1,2-diaminobenzene (1,2-DAB) and 1,4-diaminobenzene (1,4-DAB) with a reducing agent of sodium borohydride (NaBH$_4$), sequentially. The developed CQDs and magnetic nanocomposite were analyzed using FT-IR, XRD, VSM, SEM, TEM, BET surface area, BJH pore volume, and UV-Vis techniques. The results explicated that the magnetically recyclable CuFe$_2$O$_4$-CQD catalyst demonstrated high activity ($\sim$ 96.7 % conversion within 45 s, for 2-NA and $\sim$ 96.5 % conversion within 18 s, for 4-NA) and efficient recyclability (up to 5 Cycles). The pseudo-second-order apparent reaction constant rate ($k_2$) of 2-NA and 4-NA reduction were 7.12×10^{-2} and 1.77×10^{-1}, respectively. These findings reveal that the fabricated catalyst offers a new method for the simultaneous reduction of 2-nitroaniline as well as 4-nitroaniline simply for environmental safety purposes.

Keywords: Nitroanilines; Magnetic nanocomposite; Wastewater treatment; Heterogenous
1. Introduction

Water and environmental pollution caused by various organic pollutants, especially nitro compounds, has become a major problem in today’s world. Among nitro compounds, 2-nitroaniline (2-NA) and 4-nitroaniline (4-NA) are considered as the most dangerous compounds for human life and aquatic animals, due to their carcinogenic effects and potential mutagenic [1-4]. On the other hand, nitroarenes are highly soluble and can remain in the water for a long time [5]. Therefore, the US Environmental Protection Agency has included 2-NA and 4-NA in its list of toxic pollutants and hazardous waste [6, 7]. Today, nitroarenes in wastewater are mainly treated by physical, biological, and chemical techniques. Physical methods cannot totally eliminate nitroarenes, resulting in more pollution [8]. Also, biodegradation often releases large amounts of toxic intermediates into the environment. Among these methods, the chemical reduction can easily convert these toxic compounds into amino compounds that are less toxic or non-toxic [9]. Chemical reduction methods generally require metal nanocatalyst with high catalytic activity to catalyze the reduction of organic compounds [5]. Furthermore, the catalytic reduction product of 2-NA and 4-NA are 1,2-diaminobenzene (1,2-DAB) and 1,4-diaminobenzene (1,4-DAB), respectively, which are the significant intermediates for fabricating different products. For instance, aramid textile fibers, developing agents, polymers, dyes, rubber antioxidants and surfactants [1, 10].

Nano-sized catalysts have attracted much attention due to their promising characteristics, such as high surface area, porous structure, improved morphology, better distribution, and high durability [11-15]. Over the past few decades, one of the most extremely studied materials in nano formulations is CuFe$_2$O$_4$ nanoparticles [16]. Copper ferrite nanoparticles have been synthesized via various techniques, including solvothermal, ultrasonication, sol-gel, hydrothermal, and ball milling [17, 18]. CuFe$_2$O$_4$ has recently been considered due to its optical, magnetic, cost-effectiveness, and superior catalytic properties [19]. With the addition of carbon quantum dots (CQDs), the catalytic properties of metal ions increase [20]. CQDs have gradually attracted the attention of many researchers in recent years due to their advantages, such as low toxicity, low cost, and abundance in nature. In addition, CQDs also have properties that are superior to high
solubility in aqueous solutions, in terms of biocompatibility, ease of modification, and strong volumetric performance [21]. Nanocomposites, especially nanocomposites with quantum dots of carbon, have better catalytic properties than nanoparticles because aggregation occurs during the catalytic process due to their high surface energy, which affects their catalytic activity and experimental reproducibility [22, 23].

Numerous studies have been conducted on reducing 2-NA and 4-NA as a model of organic pollutants. For example, the catalytic impact of CoMn$_2$O$_4$/APTPOSS@FPS NPs was investigated by Chen et al. [24] to remove the organic pollutants from water sources as well as the environment. They stated that the prepared catalyst considerably affects a reduction of 2-NA with a conversion ratio of about 99%. Zelekew et al. [6] scrutinized the composites SiO$_2$@CuxO@TiO$_2$ as a catalyst for the reduction of 4-nitrophenol as well as 2-NA. The outcomes demonstrated that it took 150 s to convert the 2-NA. An efficient and easily recoverable Pd/CoFe$_2$O$_4$/chitosan hybrid nanocatalyst was fabricated and characterized to reduce 2-NA with NaBH$_4$ by Baran et al. [1]. The outcomes exhibited that the nanocatalyst greatly reduced 2-NA as a model of nitroaromatic compounds with a reaction time of more or fewer 65 s and 98%, sequentially. Bhaduri et al. [25] conducted a study to evaluate the effect of (Au/SiO$_3$/Fe$_3$O$_4$) composite as a catalyst on the reduction of nitroarenes including 4-nitrophenol (4-NP) and 2-nitroaniline (2-NA). Their findings showed that gold nanocomposites could remarkably reduce 2-NA with a conversation percent, time, and constant rate of 100%, 225 s, and 4.1×10$^{-3}$ s$^{-1}$, respectively. Abay et al. [26] examined the effect of different V-Bi$_2$ (O, S)$_3$ oxysulfide catalysts on reducing 2-NA by reducer agent of sodium borohydride. The 20% V-Bi$_2$ (O, S)$_3$ oxysulfide catalyst demonstrated the highest activity and fast reaction time among other synthesized catalysts with a $K_{app}$ of 34.40×10$^{-3}$ s$^{-1}$. Gupta et al. [27] investigated the effect of gold nanoparticles by synthesizing selective gold nanoparticles using the microwave synthesis technique in 6 minutes. They found that gold nanocubes could reduce 4-NA in 6 minutes and represented promising reusability for at least four cycles. The dependence of catalyst activity on synthesized nanocatalysts was also confirmed in their study. Yulizar et al. [28] assessed the SiO$_2$/NiFe$_2$O$_4$ nanocomposites’ effect on the reduction of 4-NA by using NaBH$_4$ as a reducing agent. The outcomes confirmed its great catalytic effect on the reduction with a reduction percent and time of within 95% and 30 min. Revathi et al. [29] evaluated the performance of nanocatalyst for reducing 4-NA to 1,4-DAB by synthesizing easy and low-cost copper-CuO nanocomposites to reduce nitroarenes. The results showed that the prepared
nanocomposite (Cu-CuO) revealed greater and faster catalytic properties for reducing 4-NA to 1,4-DAB than Cu and CuO.

Considering the conducted literature survey, in previous research, the raw materials used in synthesizing catalysts are mostly expensive, rare, and valuable materials that are often unavailable or difficult to find. On the other hand, those catalysts that have responded well are nanocomposites in which many raw materials have been used, or their synthesis method is time-consuming and tedious. However, none of the studies have been carried out on the effect of synthesized CuFe₂O₄-CQD nanocomposite to reduce nitroanilines (2-NA and 4-NA), which has both facile and fast synthesis methods as well as cheap and available raw materials.

In this study, the catalytic performance of in-situ synthesized glucose-derived CuFe₂O₄-CQD magnetic nanocomposite via simple hydrothermal method was evaluated. It was then used as an effective and desirable nanocomposite to reduce 2-NA and 4-NA and convert it into a valuable material of 1,2-DAB and 1,4-DAB, sequentially. The prepared nanocatalyst was characterized by employing a comprehensive characterization technique. In the final stage, the recycling of the prepared nanocatalyst was investigated.

2. Experimental section
2.1 Materials and Method

2-nitroaniline (C₆H₆N₂O₂) and 4-nitroaniline (C₆H₆N₂O₂) as models of organic pollutants, Glucose (C₆H₁₂O₆), Ethanol (C₂H₅OH), and Sodium borohydride (NaBH₄) as a reducer agent were employed in this explore. All the compounds, without any purification process, were procured from Merck company (Germany).

In order to prepare a well-dispersed solution during the reaction and to prevent aggregation, a magnetic stirrer (Fan Azma Gostar, Iran) was utilized. A detailed study of the functional groups of CQDs derived from glucose and CuFe₂O₄-CQD nanocomposite was recorded by Fourier transform infrared spectroscopy (Nexus infrared spectroscopy (Nicolet Co, USA)). To calculate the size and crystal structure of the magnetic nanocomposite, X-ray diffraction (XRD, PW1730, Philips, Netherlands) was performed at room temperature with Cu-Kα radiation (λ = 1.54056 Å). The pattern, which XRD recorded, was measured between an angle radius (2θ) of 10-80°. To calculate the crystal size of the CuFe₂O₄-CQD nanocomposite, the Debye-Scherrer formula was
used (Eq. 1) [30-32].

\[ D = \frac{k \lambda}{\beta \cos \theta} \] (1)

Where \( D_{\text{avg}} \) is the crystal size of NPs (nanometer), \( k \) is a constant (approximately 0.94 for acquired particles), \( \lambda \) is the wavelength of X-ray, \( \beta \) is the whole width at half-maximum (FWHM) of extreme and wide peaks, \( \theta \) is the angle of the Bragg’s or diffraction. The prepared nanoparticles’ diameter and morphology were characterized with scanning electron microscopy (SEM, Carl Zeiss 1430VP L, Germany) and transmission electron microscope (TEM, EM 208S, Philips, Netherlands). Centrifuge (Hettich Centrifuge EBA III) was used to aid the separation process. Finally, UV spectra (UV-Vis, Specord 250, Analytik Jena) were employed to calculate the absorption during the catalytic reduction of the mentioned nitroarenes (2-nitroaniline and 4-nitroaniline). To evaluate the magnetic properties of the synthesized samples in a magnetic field of \( \pm 60 \) kOe, a vibrating sample magnetometer (VSM) (QD-MPMS SQUID magnetometer) was utilized. The magnetization as a function of temperature (M-T curves) was recorded in the temperature range of 10-380 K. Physical adsorption and desorption of \( \text{N}_2 \) at 77 K with BELSORP MINI II device was used to measure the BET surface area and pore volume distribution of BJH of the synthesized sample.

2.2 Synthesis of Copper ferrite nanoparticles

\( \text{CuFe}_2\text{O}_4 \) nanoparticles were synthesized via the facile one-step hydrothermal method. Initially, 0.574 g of tetrasodium EDTA salt as a chelator was dispersed in 50 mL of deionized (DI) water for 10-15 minutes in an ultrasonic bath cleaner. Then, the stoichiometric amount of 3.24 g of anhydrous \( \text{FeCl}_3 \) and 1.35 g of \( \text{CuCl}_2\cdot2\text{H}_2\text{O} \) were added to the desired solution under constant stirring speed. The alkaline solution, prepared by adding 17.7 g of granular sodium hydroxide per 100 mL of water, was added dropwise to the solution using a syringe (during the reaction, the pH of the reaction was continuously monitored using a pH meter). When the pH reached 10-11, the solution was poured into a Teflon autoclave at 185 °C for 15 h. After the completion of the reaction by a strong external magnet, the magnetic sediment was separated and washed several times with ethanol and distilled water. Finally, the prepared brown sediment was dried at 60 °C for approximately 3-4 hours.
2.3 Synthesis of glucose-CQDs

Carbon quantum dots of glucose were fabricated by a facile and fast hydrothermal technique seen in Fig. 1. To synthesize quantum dots of carbon by one-pot hydrothermal method, 0.995 g of glucose was added to 65 ml of deionized water and then sonicated for about 10 minutes. Afterward, the solution was transferred to a 150 ml Teflon autoclave at 180 °C for about 4 hours. After the reaction cooled, the solution was separated with a centrifuge for 20 minutes at 7 rpm. Finally, the solution was dried in an oven at 50 °C for 8 hours. Finally, a brown viscous substance was acquired.

2.4 Synthesis of CuFe₂O₄-CQD magnetic nanocomposite

The desired magnetic nanocomposite was synthesized and prepared in situ. The hydrothermal
method with a weight ratio of 1:10 was employed to fabricate this nanocomposite. For this purpose, about 0.025 g of CuFe₂O₄ and 0.25 g of glucose were added to 35 ml of water and sonicated for 5 minutes. The solution was then transferred to a 50 ml Teflon autoclave at 180 °C for 5 hours. After the reaction, the precipitate was washed several times with water and ethanol and separated with a strong external magnet. Finally, the precipitate was dried at 50 °C in an oven for approximately 3 hours. At the end of the work, a solid brown precipitate was obtained.

2.5 The catalytic activity of CuFe₂O₄-CQD nanocomposite as a nanocatalyst

For the intended catalytic reaction, the dissolve 10 mg of each nitroaromatic compound in 50 ml of deionized water was sonicated for 15 minutes. Then, 5 ml of the nitro solution was poured into the test tube, and about 100 mg of sodium borohydride, and 7 mg of nanocatalyst were added. To measure adsorption, 100 μL of the sample was taken, transferred to the cuvette, and diluted to 3 ml. A UV-Vis spectrophotometer was utilized to investigate the reduction of nitroaromatic compounds to amino aromatic compounds, and its adsorption was investigated.

3. Results and discussion

3.1 Characterization

Fourier-transform infrared spectroscopy was monitored to investigate the functional groups of CQDs of glucose and CuFe₂O₄-CQD nanocomposite. In Fig. 2a, it is quite clear that a wide peak at approximately 3400 cm⁻¹ was attributed to the O-H stretching vibration. Strong peaks of about 1750 cm⁻¹ and 1600 cm⁻¹ are represented the metal-OH (Fe-OH and Cu-OH) bending vibration, respectively [33, 34]. In addition, the high-frequency band ~594 cm⁻¹ refers to Fe-O deformation in octahedral and tetrahedral sites. In comparison, the lower frequency band ~451 cm⁻¹ is attributed to Fe-O deformation at the octahedral hematite site, which are the functional groups of copper ferrite present in the CuFe₂O₄-CQD nanocomposite [35]. At all peaks, it can be seen that the nanocomposite peak intensity is lower than the previously reported nanoparticles. This may be due to the formation of the composite and the overlap of quantum dots and magnetic CuFe₂O₄ nanoparticles.

As shown in Fig. 2b, the wide peak between 3500-3300 cm⁻¹ was allocated to the O-H vibration bond. The weak bond at approximately 2900 cm⁻¹ was ascribed to the C-H stretching bond. The
seen at 1500 cm\(^{-1}\) was associated with the C=O vibration strength bond. The bonds from 1500 to 1350 cm\(^{-1}\) were attributed to the C-O-H and O-C-H vibrations. A band seen in a plane formation at 1100 cm\(^{-1}\) corresponded to C-H and O-H deformation. The peak from 1100 to 900 cm\(^{-1}\) was assigned to the stretching bond of C-C and C-O stretching. The bend vibration of C-H aromatic, exists in glucose structure, is seen in the 835 cm\(^{-1}\) [36].

Fig. 2. FT-IR spectra of: (a) CuFe\(_2\)O\(_4\)-CQD nanocomposite; (b) glucose-CQDs.

XRD technique was used to determine the size of nanoparticles, crystal structures, and material purity Fig. 3 [37]. shows the XRD pattern of CuFe\(_2\)O\(_4\)-CQD nanocomposite. All diffraction peaks can be indexed to the CuFe\(_2\)O\(_4\) tetragonal phase (JCPDS card (34-0425)). Characteristic diffraction peaks at 2\(\theta\) values of 30.09°, 35.69°, 43.49°, 57.44°, and 62.89° indicate the (112), (211), (220), (321), and (400) crystal planes of CuFe\(_2\)O\(_4\), respectively (tetragonal shape) [38]. Some secondary impurities, such as Fe\(_2\)O\(_3\), were still found at 2\(\theta\) values of 33.19° and 40.94°, which is in good acceptance of the JCPDS card (33-0664), may be attributed to the insolubility of FeO [39, 40]. In addition, the nanocomposite’s XRD pattern confirms the nanocomposite’s crystal structure. A
broad diffraction peak at 2θ of 22.5° was attributed to the (002) peak, indicating that the CQDs were added to the magnetic CuFe$_2$O$_4$ nanoparticles. According to the crystal plane (211), the size of the nanoparticles was calculated to be about 17 nm based on Scherer’s equation [41]. A prominent peaks seen at 2θ=49.54° (202), 54.14° (020), 74.64° (220) corresponding to the monoclinic CuO phase plane (JCPDS No. 80-1916) [42, 43].

![XRD patterns of CuFe$_2$O$_4$-CQD nanocomposite.](image)

**Fig. 3.** XRD patterns of CuFe$_2$O$_4$-CQD nanocomposite.

Scanning electron microscopy and transmission electron microscopy were used to obtain more information about the morphology and size of the prepared nanoparticles. The TEM images are shown in **Fig. 4a, b**, SEM pictures are depicted in **Fig. 4c, d**, and EDX mapping images are demonstrated in **Fig. 5** for CuFe$_2$O$_4$-CQD magnetic nanocomposite samples. TEM analysis was performed to obtain more information on the morphology of the nanocomposite as a catalyst. It is observed from **Fig. 4a, b** that some nanoparticles were agglomerated, which can be due to the large specific surface area, small particle size, and high surface energy of CuFe$_2$O$_4$ nanoparticles. As the surface-to-volume ratio of nanoparticles increases, the effect of the catalyst rises.

The results acquired from the SEM images reveal that the particle diameter size was approximately 15.30 nm with high spherical aggregation and cubic shape. The cause of nanoparticle aggregation was related to the interaction between copper ferrite magnetic
nanoparticles, solution irradiation time, and magnetic particle formation [44]. As a result, the reaction speed and time of the nanocomposite individually were higher than that of CuFe$_2$O$_4$ nanoparticles. In addition, the EDX mapping pictures represent the elements Cu, C, O, and Fe that were completely distributed throughout the CuFe$_2$O$_4$-CQD nanocomposite. The nanocomposite map fully shows the homogeneous distribution of these elements.

**Fig. 4.** (a, b) TEM and (c, d) SEM image of CuFe$_2$O$_4$-CQDs.
Corresponding magnetic measurements of CuFe$_2$O$_4$-CQD nanocomposite, which were performed in the magnetic field in the range of -60 to +60 kOe (M-H hysteresis loop), proved their satisfactory saturation magnetization ($M_s$) and favorable superparamagnetic properties (Fig. 6). The $M_s$ value of CuFe$_2$O$_4$-CQD nanocomposite was 42.76 emu g$^{-1}$ without observing apparent remanence and coercivity. Such nanocomposites can be rapidly assembled by an external magnetic field, providing multifunctional properties for separation and reduction processes. Because the average particle size of this sample was less than 20 nm and showed reversible hysteresis curves with negligible retention and coercivity, the sample could exhibit superparamagnetic behavior [45]. The Hc for CuFe$_2$O$_4$-CQD nanocomposite was 0.7 Oe.

It has been reported that the lower magnetization in nanoparticles is due to surface spin caused
by competitive antiferromagnetic interactions. Lower magnetization can also be caused by the unsaturation of small arbitrarily dispersed particles that exhibit high crystal magnetic anisotropy. Other reasons were considered to justify the lower magnetization in nanoparticles, such as creating a passive magnetic layer, spin glass properties, and irregular cation distribution on the surface of nanoparticles [46].

**Fig. 6.** VSM curve of CuFe$_2$O$_4$-CQD nanocomposite.

**Fig. 7** indicates the magnetic separation of superparamagnetic nanoparticles of CuFe$_2$O$_4$-CQD. **Fig. 7a** shows the p-NA solution. After adding the synthesized nanocatalyst, the reaction commenced. To demonstrate the magnetic properties of the prepared catalyst, the reaction was detached with external strong magnetic (**Fig. 7b**). To illustrate the detailed separation stage to preparing the catalyst for recovery level, the oval magnetic (**Fig. 7c**) and external magnetic separately was utilized (**Fig. 7d**). These photographs confirmed the superparamagnetic properties of CuFe$_2$O$_4$-CQD nanocomposite as a magnetic catalyst, which is in the acceptance with VSM analysis.
Fig. 7. The magnetic property (a) before reaction, (b) after adding catalyst, (c) after the separation of catalyst using an oval magnet, and (d) using an external magnet.

Based on the BET and BJH tests, the surface area of 23.5 m$^2$/g, pore volume of 0.05 cm$^3$/g, and mean pore diameter of 8.1 nm were acquired for CuFe$_2$O$_4$-CQD nanocomposite (Table 1). The reported values showed that CuFe$_2$O$_4$-CQD nanocomposite had nano-scale porosity accompanied by mesoporous structure [47, 48].

<table>
<thead>
<tr>
<th>Table 1. Structural and textural properties of CuFe$_2$O$_4$-CQD nanocomposite.</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET surface area (m$^2$/g)</td>
</tr>
<tr>
<td>----------------------------</td>
</tr>
<tr>
<td>23.5</td>
</tr>
</tbody>
</table>

To distinguish the CuFe$_2$O$_4$-CQD texture properties, the N$_2$ adsorption/desorption isotherm of CuFe$_2$O$_4$-CQD is plotted in Fig. 8. According to the reported trend for CuFe$_2$O$_4$-CQD isotherm, it can be noted that its trend is classified as II mode and H4 hysteresis. This mode and hysteresis confirmed the mesopores-containing texture of CuFe$_2$O$_4$-CQD nanocomposite. Additionally, narrow mesopores are erratically scattered in inner zones.
**Fig. 8.** N\textsubscript{2} adsorption/desorption isotherm of CuFe\textsubscript{2}O\textsubscript{4}-CQD nanocomposite.

As expected according to the N\textsubscript{2} adsorption/desorption isotherm, the BJH pore diameter distribution of CuFe\textsubscript{2}O\textsubscript{4}-CQD nanocomposite illustrated in **Fig.9** indicated that porous CuFe\textsubscript{2}O\textsubscript{4}-CQD nanocomposite contains the mesopores, mainly with small diameters. There was no attendance of macropores and a minor number of big mesopores. As a result, CuFe\textsubscript{2}O\textsubscript{4}-CQD nanocomposite could be recognized as a mesoporous structure.
3.2 UV-Vis examination

Reduction of nitroanilines (NAs), including 2-NA and 4-NA with NaBH₄ as a reductant exploited in the presence and absence of nanocatalyst, are exhibited in Fig. 10. The UV-Vis spectrum showed a gradual decrease at the typical absorption peak at 380 nm, in which only 3% of the NAs decreased after 24 h [49]. Therefore, it indicates that a kinetic barrier may inhibit the electron transfer from the NaBH₄ as an electron donor to the NAs receptor. The catalytic activity of CuFe₂O₄-CQD nanocomposite as a heterogeneous catalyst catalyzed the reduction of 2-NA to 1,2-DAB and 4-NA to 1,4-DAB in the presence of NaBH₄. In order to examine the reduction of 2-NA, two main peaks are observed at $\lambda_{\text{max}} = 286$ nm and 418 nm (Fig. 10a, c). Over time, as can be seen in Fig. 10c, the absorbance decreased from 0.617 to 0.024 at $\lambda_{\text{max}} = 418$ nm and changed from 286 nm to 293 nm. The main reason for the declination was related to the decrease in 2-NA concentration, and the shift was due to the formation of 1,2-DAB [1]. The adsorption peak was examined for 4-NA at $\lambda_{\text{max}} = 390$ nm (Fig. 10b, d). In the reduction assessment, Fig. 10a, b represented that there was no reaction even for hours when only sodium borohydride reducing agent was added to the solution before adding the nanocatalyst. However, after adding the magnetic catalyst, as revealed in Fig. 10d, the adsorption at $\lambda_{\text{max}} = 390$ nm for 4-NA decreased.
from 1.33 to 0.044. During this process, the new absorption peak observed at approximately 310 nm, began to increase after 18 seconds. This decrease at 390 nm was related to the decrease in 4-NA concentration, and the increase and new peak were related to creating a new amine product, 1,4-DAB [50]. In order to describe the reduction process, as shown in Fig. 11, the outcomes exhibited that effective electron transfer from the \( BH^- \) anion to nitroanilines (2-NA and 4-NA) as electron receptors occurs by the fermi surface shift of the nanoparticles, representing its remarkable catalytic activity. The catalyst’s performance depends on the available active surface and the number of active sites on the surface. In addition, as the nanomaterial reacts with the \( BH^- \) anion, a hydride can form and subsequently interact with nitroaniline molecules that may be adsorbed on the metal surface. As a result, after a rapid reaction at the active sites, the reaction was completed rapidly, while the product was expelled from the nanomaterial surface almost immediately [49]. Fig. 12 illustrates the color change during reduction. It is evident that the color of PNA and ONA is bright yellow and orange-yellow solid; sequentially, after adding reductant, there are no changes in color, but after adding as-synthesized nanocatalyst, the color changed to colorless (gray) [26, 29].
Fig. 10. UV-Vis spectra of (a) 2-NA and (b) 4-NA after adding NaBH₄ solution without any catalyst; the successive reduction of (c) 2-NA to 1,2-DAB and (d) 4-NA to 1,4-DAB after adding the CuFe₂O₄-CQD nanocomposite as a promising catalyst.
Fig. 11. Proposed mechanism for the reduction of 4-NA and 2-NA in the presence of reducer and CuFe$_2$O$_4$-CQD nanocomposite.

Fig. 12. Reduction of 4-nitroaniline and 2-nitroaniline with colour changes from yellow to colourless inside.
The effectiveness of CuFe$_2$O$_4$-CQD nanocomposite as a catalyst for reducing 2-NA and 4-NA was calculated by Eq. 2. In this formula, $A_0$ and $A_t$ are considered to be the absorbance of the solution at time=0 (absorption of 2-NA or 4-NA without any additives) and time=t, consequentially [51, 52].

\[
\text{(\% Conversion)} = \frac{A_0 - A_t}{A_0} \times 100
\] (2)

A correlation between $\ln \left( \frac{C_t}{C_0} \right)$ and reduction time ($t$) for the reduction of 2-NA and 4-NA using CuFe$_2$O$_4$-CQD magnetic nanocatalyst is observed clearly in Fig. 13. Since the concentration of the reducer (NaBH$_4$) is higher than the NAs used, the catalytic system follows pseudo-first-order kinetics. The following equation was used to calculate the constant rate ($K_{app}$):

\[
\ln \left( \frac{C_t}{C_0} \right) = \ln \left( \frac{A_t}{A_0} \right) = -K_{app} \cdot t
\] (3)

In the considered equation, the definition of all parameters is the same as the Eq. 2, $t$ at any given time, and $K_{app}$ is the apparent constant rate [1, 53].

The pseudo-first-order kinetic reaction equation shows the unfavorable quality of the linear fit in 4-NA and 2-NA samples as shown in Fig. 13a, d. In contrast, the data can be completely fitted by a pseudo-second-order kinetic reaction equation, shown below.

\[
\frac{1}{c} - \frac{1}{c_0} = K_2 \cdot t
\] (4)

where $K_2$ (L mg$^{-1}$ min$^{-1}$) is the second-order kinetics rate constant, and was determined from a linear fit to the data [54].

To calculate the constant rate in more detail ($k'$) for the amount of catalyst used to catalyze the reaction by the obtained nanocatalyst, equation. 4 can be used:

\[
k' = \frac{K_{app}}{m}
\] (4)

In Eq. 4, $k'$ is equal to the ratio of $K_{app}$ that could be considered s$^{-1}$ or min$^{-1}$ to $m$ (the exact catalyst dosage (g or mg) was utilized to catalyze the 2-NA or 4-NA solution reduction [55]. By using Eq. 2, 3, and 4, the conversion percent, apparent rate constant, and rate constant per catalyst unit were calculated, which are listed in Table 2.
**Table 2** Reduction results of magnetic promising catalyst for 2-nitroaniline and 4-nitroaniline.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Nitroaniline</th>
<th>Conversion (%)</th>
<th>$R^2$</th>
<th>$K_2$ (s⁻¹)</th>
<th>$k'$ (s⁻¹.mg⁻¹)</th>
<th>Time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuFe₂O₄-CQD</td>
<td>2-NA</td>
<td>96.7</td>
<td>0.991</td>
<td>1.77×10⁻¹</td>
<td>5.07 × 10⁻²</td>
<td>45</td>
</tr>
<tr>
<td>CuFe₂O₄-CQD</td>
<td>4-NA</td>
<td>96.5</td>
<td>0.988</td>
<td>7.12×10⁻²</td>
<td>2.03 × 10⁻²</td>
<td>18</td>
</tr>
</tbody>
</table>

It can be seen in the Fig. 13a, c, the slope of the line $-\ln\left(\frac{A_t}{A_0}\right)$ versus time can be defined as $K_{app}$. By passing the time, the slope of the line slightly increased. It is noticeable in Fig. 13a, d, the concentration of substrates as a model pollutant in the aquatic environment decreased due to substrate consumption during the reduction and finally reached zero. As seen in Fig. 13c, f, according to the application of the quadratic equation, it can be seen that the graph is close to the linear.

CuFe₂O₄-CQD nanocomposite as a nanocatalyst for catalyzing the reduction reaction of 2-nitroaniline and 4-nitroaniline has been compared with other researchers reported in the same study, which can be seen in Table 3 and Table 4 respectively. Our catalyst is the best and most effective catalyst among the synthesized catalysts, which are candidates for other studies for many reasons. First, other catalysts or precursors were expensive, scarce, or a combination of several materials. These reasons cannot be ignored in terms of affordability and availability. Second, those with inexpensive raw materials also had high response times, which were not inconspicuous in terms of time savings. Hence, the obtained nanocatalyst is the best catalyst in terms of time-saving, availability of raw materials, cost-effectiveness, and easy synthesis methods.
Fig. 13. Linear dependence of $\ln \left( \frac{C_t}{C_0} \right)$ versus reaction time by CuFe$_2$O$_4$-CQDs catalyst for (a, b, c) 2-NA and (d, e, f) 4-NA.
Table 3 A comparative study for 2-NA reduction and efficiency of CuFe$_2$O$_4$-CQDs nanocomposite compared to nanocatalyst is reported.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Completion time</th>
<th>$K_{app}$</th>
<th>Reaction condition</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/CoFe$_2$O$_4$/chitosan</td>
<td>65 s</td>
<td>0.0131 (s$^{-1}$)</td>
<td>S = 1 mL, 1.25 $\times$ 10$^{-4}$ M R = 0.1 mL, 2.5 $\times$ 10$^{-2}$ M C = 4 mg</td>
<td>[1]</td>
</tr>
<tr>
<td>PVDF/microgel@Pd</td>
<td>80 min</td>
<td>0.035 (s$^{-1}$)</td>
<td>–</td>
<td>[5]</td>
</tr>
<tr>
<td>SiO$_2$@Cu$_x$O@TiO$_2$</td>
<td>150 s</td>
<td>0.025 (s$^{-1}$)</td>
<td>S = 1 mM/L (300 μL) R = 0.1 M (8 mL) C = 10 mg</td>
<td>[6]</td>
</tr>
<tr>
<td>CoMn$_2$O$_4$/APTOPSS@FPS NPs</td>
<td>100 s</td>
<td>–</td>
<td>S = 40 μL (1.26 $\times$ 10$^{-2}$ M) R = 0.5 M C = 1 mg/2.5 mL</td>
<td>[24]</td>
</tr>
<tr>
<td>Fe$_3$O$_4$@SiO$_2$-NH$_2$–Au</td>
<td>4.2 min</td>
<td>4.1 $\times$ 10$^{-3}$ (s$^{-1}$)</td>
<td>S = 0.1 mL (0.005 M) R = 1 mL (0.2 M) C = 3 mg</td>
<td>[25]</td>
</tr>
<tr>
<td>20%V-doped Bi$_2$(O, S)$_3$</td>
<td>150 s</td>
<td>34.4 $\times$ 10$^{-3}$ (s$^{-1}$)</td>
<td>S = 100 mL, 20 mg/L R = 0.1 M, 5 mL C = 10 mg</td>
<td>[26]</td>
</tr>
<tr>
<td>UiO-66-NH$_2$/TTACP/ Ni@Pd NPs</td>
<td>150 s</td>
<td>–</td>
<td>S = 1.26$\times$10$^{-2}$ mol/L R = 0.5 M C = 1 mg/2.5 mL</td>
<td>[55]</td>
</tr>
<tr>
<td>Ni@Au/KCC$^{-1}$</td>
<td>10 min</td>
<td>4.7 $\times$ 10$^{-3}$ (s$^{-1}$)</td>
<td>S = 0.126 mM R = 0.5 M C = 10.0 mg/mL (30 μL)</td>
<td>[56]</td>
</tr>
<tr>
<td>Sr/Alg/CMC/GO/Au</td>
<td>2 min</td>
<td>4.9 $\times$ 10$^{-3}$ (s$^{-1}$)</td>
<td>S = 0.1 mM (1 mL) R = 0.1 M (1 mL) C = 1 mg/mL</td>
<td>[57]</td>
</tr>
<tr>
<td>Cu/Alg./CMC/Dex. /r-GO</td>
<td>1.5 min</td>
<td>0.50 (min$^{-1}$)</td>
<td>S = 0.001 M R = 0.1 M C = 0.001 g</td>
<td>[58]</td>
</tr>
<tr>
<td>Catalyst</td>
<td>Completion time</td>
<td>( k_{\text{app}} )</td>
<td>Reaction condition</td>
<td>Ref</td>
</tr>
<tr>
<td>-----------------------------------------------</td>
<td>----------------</td>
<td>----------------------------</td>
<td>---------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>CS/GA/RGO/Pd composite</td>
<td>28 min</td>
<td>0.125 (min(^{-1}))</td>
<td>( S = (1 \text{ mL}, 5 \text{ mM}) )</td>
<td>[59]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( R = (10 \text{ mL}, 0.01 \text{ M}) )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( C = \text{NM} )</td>
<td></td>
</tr>
<tr>
<td>FeNi(_5)/DFNS/Cobaloxime/PCPL</td>
<td>140 s</td>
<td>–</td>
<td>( S = 40 \mu \text{L} \left(1.26\times10^{-2} \text{ M}\right) )</td>
<td>[60]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( R = 0.5 \text{ M} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( C = 10 \text{ mg}/2.5 \text{ mL} )</td>
<td></td>
</tr>
<tr>
<td>Ag-p (NIPMAM-co-AAc)</td>
<td>14 min</td>
<td>0.126 (min(^{-1}))</td>
<td>( S = 8 \text{mL} \left(200 \text{ ppm}\right) )</td>
<td>[61]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( R = 16.8 \text{ mM} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( C = 6.3 \text{ mg/mL} )</td>
<td></td>
</tr>
<tr>
<td>CeO(_2)</td>
<td>60 s</td>
<td>–</td>
<td>( S = 0.015 \text{ mM} )</td>
<td>[62]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( R = 0.005 \text{ M} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( C = 0.1 \text{ mg} )</td>
<td></td>
</tr>
<tr>
<td>Ag NPs</td>
<td>10 min</td>
<td>( 2.43 \times 10^{-3} \text{ (s}^{-1}) )</td>
<td>( S = 1 \text{ mM}, 1.50 \text{ ml} )</td>
<td>[63]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( R = 0.05 \text{ M}, 1.00 \text{ ml} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( C = 0.50 \text{ ml} )</td>
<td></td>
</tr>
<tr>
<td>CuFe(_2)O(_4)-CQDs (glucose)</td>
<td>45 s</td>
<td>( 1.77 \times 10^{-1} \text{(s}^{-1}) )</td>
<td>( S = 10 \text{ mg}/50\text{mL} \left(5 \text{ mL}\right) )</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( R = 100 \text{ mg} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( C = 3.50 \text{ mg} )</td>
<td></td>
</tr>
</tbody>
</table>

\( S \): substrate; \( R \): reducer (NaBH\(_4\)); \( C \): catalyst; \( k_{\text{app}} \) = apparent constant rate.

**Table 4** Comparative study for 4-NA reduction and efficiency of CuFe\(_2\)O\(_4\)-CQDs nanocomposite compared to the reported nanocatalyst.
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction Time</th>
<th>Apparent Rate Constants</th>
<th>Reaction Conditions</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag NPs</td>
<td>10 min</td>
<td>$6.22 \times 10^{-3}$ (s(^{-1}))</td>
<td>S = 1 mM, 1.50 ml, R = 0.05 M, 1.00 ml, C = 0.50 ml</td>
<td>[63]</td>
</tr>
<tr>
<td>ZnO/CdO/RGO</td>
<td>120 min</td>
<td>$7.1 \times 10^{-3}$</td>
<td>S = 10 mg/L, R = -</td>
<td>[64]</td>
</tr>
<tr>
<td>Au-NF</td>
<td>16 min</td>
<td>$1.3 \times 10^{-3}$</td>
<td>S = 1 mM/L (300 μL), R = 0.1 M/L (300 μL), C = 0.4 mmol/L (300 μL)</td>
<td>[65]</td>
</tr>
<tr>
<td>Co(_3)O(_4)</td>
<td>210 s</td>
<td></td>
<td>S = 1.8 ml, R = 1.0 ml, C = 0.02 g</td>
<td>[66]</td>
</tr>
<tr>
<td>Cu NPs/Cotton fabric</td>
<td>5 min</td>
<td></td>
<td>S = 0.025 mM, 30 ml, R = 3 M, 2.0 ml, C = 0.50 ml</td>
<td>[67]</td>
</tr>
<tr>
<td>Ag-PNiM hybrid microgels</td>
<td>13 min</td>
<td>0.0852 (min(^{-1}))</td>
<td>S = 0.060 mM, R = 26.7 mM, C = 4mg/mL</td>
<td>[68]</td>
</tr>
<tr>
<td>FeAgPt alloy NPs</td>
<td>25 min</td>
<td>$10.06 \times 10^{-2}$ (min(^{-1}))</td>
<td>S = 0.025 mM, R = 0.4 mL/ 0.2 M, C = NM</td>
<td>[69]</td>
</tr>
<tr>
<td>ZnO NPs on glass plate</td>
<td>105 min</td>
<td>0.0244 (min(^{-1}))</td>
<td>S = 10 mg/L, R = NM, C = 10 mg/L</td>
<td>[70]</td>
</tr>
<tr>
<td>CuFe(_2)O(_4)-CQDs (glucose)</td>
<td>18 s</td>
<td>$7.12 \times 10^{-2}$ (s(^{-1}))</td>
<td>S =10 mg/50mL (5 mL), R = 100 mg, C = 3.50 mg</td>
<td>This study</td>
</tr>
</tbody>
</table>

S: substrate; R: reducer (NaBH\(_4\)); C: catalyst; \(k_{app}\) = apparent constant rate.

The reusability and recyclability of the nanocatalyst in the reduction of NAs should be investigated when evaluating the catalyst applications. For this purpose, the recyclability of the magnetic catalyst in 5 repeated recycling in the reduction of 4-NA and 2-NA, as shown in Fig. 14, was evaluated. The solution was washed with ethanol and water, separated via a strong external
magnet to reactivate it, filtered with a pump, and dried after each reaction. The recovered and dried catalyst was reused in subsequent catalytic reactions. The result of the study revealed that the magnetic nanocatalyst showed a higher recyclability performance, in that the catalytic efficiency of the reusable catalyst decreased slightly from 96.7% to 89.86% for the reduction of 4-NA and dropped from about 96.5% to 88.24%. To reduce 2-NA after 5 cycles. These findings showed that CuFe$_2$O$_4$-CQD nanocomposite is an efficient and reusable catalyst for the reduction of 4-NA as well as 2-NA.

![Diagram showing reusability percentage for the reduction of 2-NA and 4-NA at different cycles.](image)

**Fig. 14.** Reusability percentage for the reduction of 2-NA and 4-NA at different cycles.

4. **Conclusion:**

   The magnetic nanocomposite of CuFe$_2$O$_4$-CQD was prepared via hydrothermal in one step using glucose. The nanoparticles showed enhanced catalytic activities in the hydrogenation of 2-nitroaniline to 1,2-DAB and 4-nitroaniline to 1,4-DAB with a significant reduction in reaction time and an increase in the rate constant due to the high number of active surface sites. The time taken for the complete conversion of 2-NA and 4-NA was 45 and 18 seconds with an apparent rate constant ($k'$) per amount of catalyst is $5.07 \times 10^{-2}$ and $2.03 \times 10^{-2}$, respectively. In addition, the catalyst was removed after the completion of the reaction using an external magnet. It is then
purified and recycled for further reactions with a slight decrease in activity. Furthermore, these reduction reactions are achieved in an aqueous environment, which makes them more economical, environmentally friendly, and easier to work with. The outcomes revealed that the prepared nanocatalyst is very useful in protecting the environment, especially the pollution of natural water sources from industrial effluents.

**Author contribution**

**Samin Naghash-Hamed**: Investigation, Conceptualization, Methodology, Formal analysis, Writing original draft. **Nasser Arsalani**: Supervision. **Seyed Borhan Mousavi**: Formal analysis, Writing original draft.

**Ethical approval**

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**Data availability**

All data generated or analysed during this study are included in this published article.

**Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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