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An efficient method for the preparation of magnetic Co_3O_4 nanoparticles and the study of their catalytic application

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In this study, magnetic cobalt oxide (Co_3O_4) nanoparticles (NPs) were synthesized through a new and green method using cobalt chloride hexahydrate ($CoCl_2.6H_2O$), pluronic P123 as a stabilizer, and sodium borohydride ($NaBH_4$). The CO_3O_4 nanoparticles were characterized by diffuse reflectance infrared Fourier transform spectroscopy, powder X-ray diffraction, X-ray photoelectron spectroscopy, energy-dispersive X-ray spectroscopy, scanning electron microscopy, and vibrating sample magnetometer.

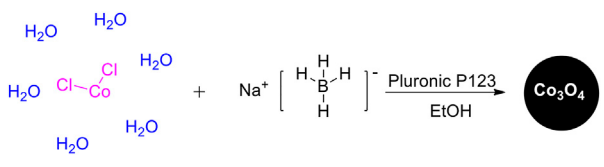
The magnetic Co_3O_4 NPs were used as a catalyst with high activity and stability in the synthesis of tetrahydrobenzo[b]pyran derivatives. This reaction was carried out in water, as it is an environmentally friendly solvent, using a low loading of Co_3O_4 NPs at room temperature. Various derivatives of aldehydes were used as substrates to obtain a high yield of the corresponding tetrahydrobenzo[b]pyrans in short times. In addition, the catalyst was recovered and reused several times with no notable decrease in its activity.

KEYWORDS

magnetic cobalt oxide, nanoparticles, tetrahydrobenzo[b]pyrans, recoverable nanocatalyst, Biologically active compounds

1 Introduction

In the last decade, magnetic nanoparticles (MNPs) have been noted by many researchers owing to their advantages of high stability, magnetic and electrical properties, high surface area, and special optical properties (Ichiyanagi et al., 2004; Zhang et al., 2006; Bisht and Rajeev, 2011; Ghasemzadeh et al., 2017; Ramamoorthy and Rajendran, 2017; Yin et al., 2017; Vennela et al., 2019). Among different magnetic nanoparticles, cobalt oxide (Co_3O_4) NPs are very interesting due to their high chemical stability, good reactivity, high surface area, excellent semiconductivity, easy synthesis, high catalytic performance, and superior magnetic properties. These nanoparticles have many applications, such as in energy storage, sensors, anodic supplies, drug delivery, and catalysis (Kumar et al., 2008; Koza et al., 2012; Wang et al., 2015; Agilandeswari and Rubankumar, 2016; Ivetić et al., 2016; Pourzare et al., 2017; Galini et al., 2018; Shi et al., 2019; Tahanpesar et al., 2019; Mohammadi et al., 2020; Tonelli et al., 2020; Al-Qasmi, 2022; Anele et al., 2022; Bilge et al., 2022; Farrag and Ali, 2022; Mohammadpour-Haratbar et al., 2022; Saeed et al., 2022). The chemical formula of these NPs is $Co^{2+}(Co^{3+})_2O_4$ with a normal spinel structure in which Co^{2+} ions are in tetrahedral interstices and Co^{3+} ions are in the octahedral interstices of the cubic close-packed lattice of oxide anions (Salavati-Niasari et al., 2009; Thota et al., 2009). It is believed that the shape and size of NPs affect their properties; thus, the morphology of these



SCHEME 1
Preparation of Co_3O_4 nanoparticles.

nanoparticles must be controlled. Co_3O_4 NPs have been synthesized in various morphologies such as nanorods (Lou et al., 2007; Meng et al., 2015), nanotubes (Chen et al., 2015; Wang et al., 2019), nanowires (Mahmoud and Al-Agel, 2011; Yao et al., 2012), cubic (Ghiasi et al., 2016; Liu et al., 2020), spheres (Chen et al., 2007; Wang et al., 2017), and mesoporous (Qiu et al., 2014; Zhao et al., 2019). Since Co_3O_4 NPs and their nanocomposites are resistant to corrosion, they have been used as powerful catalysts in different chemical reactions. Some recent reports in this matter are Co_3O_4–SiO_2 nanocomposites for CO oxidation (Jia et al., 2011), Co_3O_4@SiO_2 NPs for the preparation of 3,4-dihydroquinoxalins (Ghasemzadeh et al., 2016), Co_3O_4 for the reduction of 4-nitrophenols (Al Nafiey et al., 2017), Co_3O_4@SiO_2 for the preparation of indazoles (Ghasemzadeh et al., 2017), Co_3O_4 NPs as a photocatalyst for methylene blue degradation (Vennela et al., 2019), and Co_3O_4@SiO_2 core/shell–nylon as an adsorbent for the removal of Congo red from wastewater (Mohammadi et al., 2020). There are also several methods for the synthesis of these NPs, including sol–gel, chemical pyrolysis, microemulsion, chemical vapor deposition (CVD), coprecipitation, microwave, decomposition of organic precursors, and hydrothermal methods (He et al., 2004; Yoshikawa et al., 2004; Ştefănescu et al., 2008; Ozkaya et al., 2009; Gupta et al., 2011; Alagiri et al., 2013; Salavati-Niasari and Khansari, 2014; Gopinath et al., 2016; Diallo et al., 2017; Izu et al., 2017; Jamil et al., 2018; Tan et al., 2018; Yetim, 2021). However, some of the aforementioned methods face problems of high reaction temperature, high pressure, and the use of expensive precursors. Therefore, designing a novel method to overcome the aforementioned limitations is an important subject in this matter.

On the other hand, multicomponent reactions are one of the very important chemical processes because of their key role in the synthesis of biologically active heterocyclic organic compounds (Fotouhi et al., 2007; Altass et al., 2021; Alshorifi et al., 2022; Altass et al., 2022; El-Yazeed et al., 2022). Tetrahydrobenzo[b] pyrans are one of these compounds that are synthesized *via* a three-component reaction. They have good biological activity and are used in the pharmaceutical field, cosmetics, agriculture, pigment, etc. (Hekmatshoar et al., 2008). To date, many catalysts have been reported for the preparation of tetrahydrobenzo[b] pyrans. Some of the recently developed catalysts are choline hydroxide-based ionic liquid [Ch][OH] (Hu et al., 2014), nano-structured diphosphate ($Na_2CaP_2O_7$, DIPH) (Maleki et al., 2016), dihydrogen phosphate-supported silica-coated magnetic nanoparticles (H_2PO_4–SCMNPs) (Saadati-Moshtaghin and Zonoz, 2017), Fe_3O_4@Ph–SO_3H (Elhamifar et al., 2018), Preyssler heteropoly acid on $Ni0.5Zn0.5Fe_2O_4$ magnetic nanoparticles (MNPs) (Javid and Moeinpour, 2018), nickel Schiff base complex immobilized on silica-coated Fe_3O_4 (Fe_3O_4@SiO_2@NiSB) (Maleki et al., 2020), and Eu/IDA/CPTS@ $CoFe_2O_4$ (Tamoradi et al., 2020).

In view of the aforementioned characteristics, herein, for the first time, a novel surfactant-assisted method is presented for the

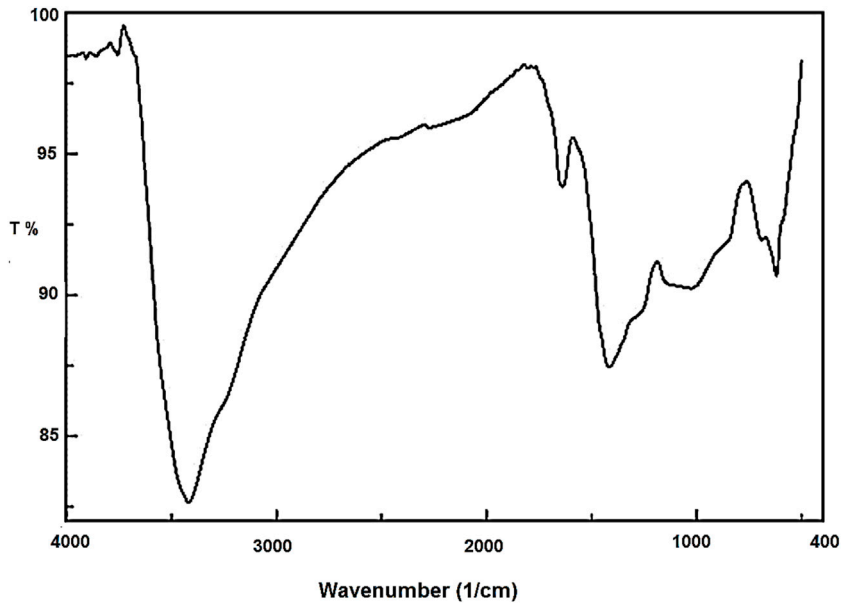


FIGURE 1
FT-IR spectrum of the Co_3O_4 NPs.

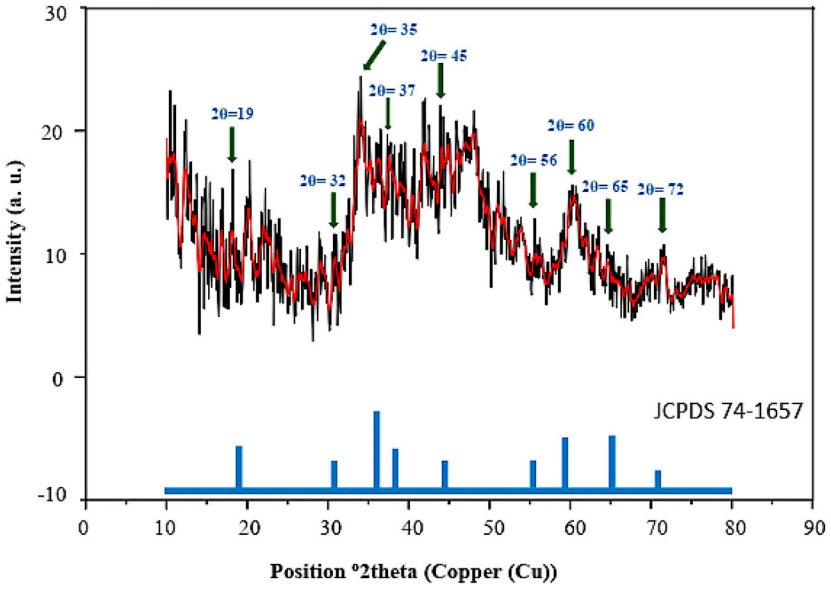


FIGURE 2
PXRD pattern of the Co_3O_4 NPs.

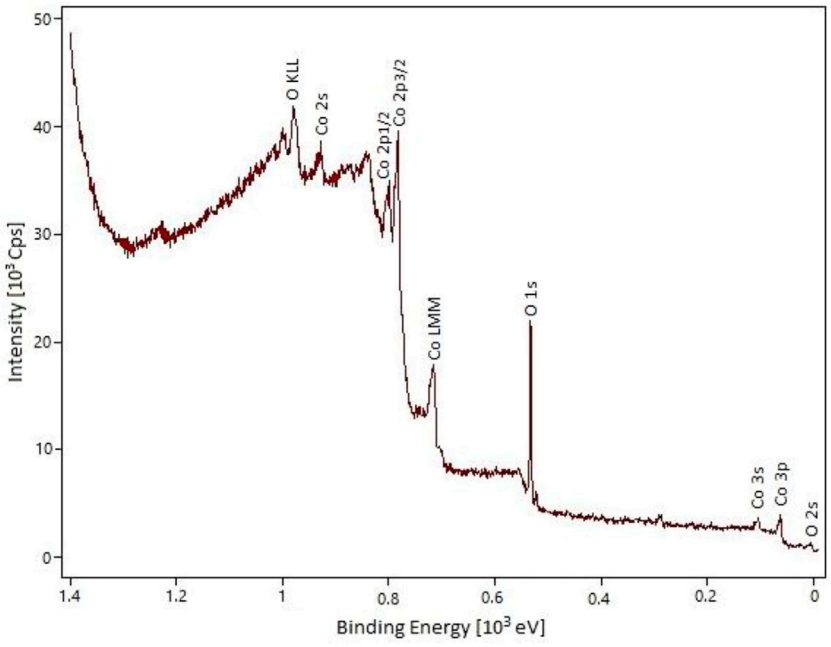


FIGURE 3
XPS analysis of the Co_3O_4 NPs.

preparation of magnetic cobalt oxide nanoparticles. In this method, $NaBH_4$ has been used as a reducing agent and the pluronic P123 surfactant has been employed as a stabilizer. Moreover, the reaction was performed in EtOH at room temperature. The Co_3O_4 NPs were characterized and employed as a powerful nanocatalyst in the synthesis of tetrahydrobenzo[b]pyrans.

2 Experimental

2.1 General

All chemicals were used as received with no further purification. Pluronic P123 (98%), $CoCl_2.6H_2O$ (98%), malononitrile (≥99%),

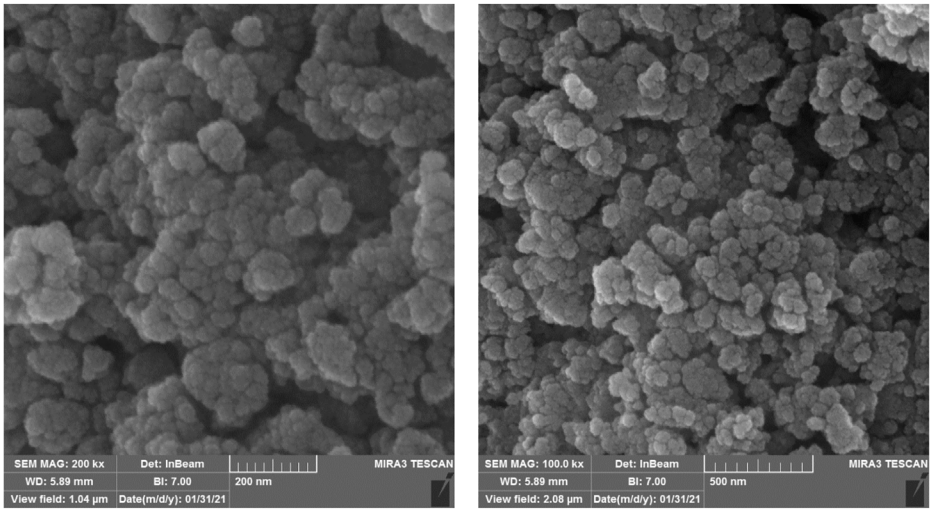


FIGURE 4
SEM images of the Co_3O_4 NPs.

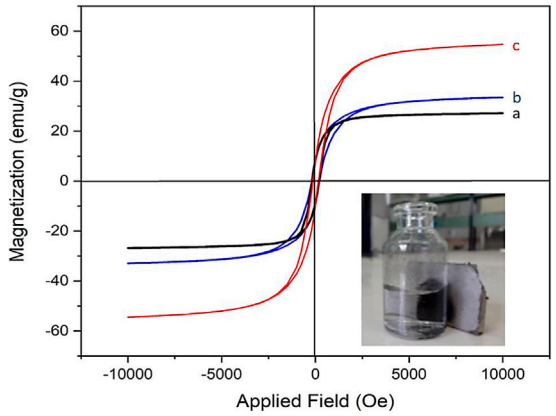


FIGURE 5
VSM diagrams of Co_3O_4 NPs prepared *via* **(A)** the milling process, **(B)** EtOH/$NaBH_4$, and **(C)** EtOH/$NaBH_4$/pluronic P123 methods. Magnetic separation of Co_3O_4 NPs (inset figure).

and dimedone (95%) were purchased from Sigma-Aldrich. Moreover, aldehydes (≥95%) and sodium borohydride (99%) were purchased from Merck. Powder X-ray diffraction (PXRD) was performed using a Bruker D8 ADVANCE diffractometer (Germany). The morphology of the particles was evaluated using the TESCAN-Vega3 scanning electron microscope (SEM) (Czech Republic). Energy-dispersive X-ray (EDX) spectroscopy was performed using the TESCAN-Vega3 apparatus (Czech Republic). Fourier transform infrared (FT-IR) spectroscopy was recorded on a Bruker Vector 22 spectrometer (Germany). The magnetic properties of the particles were investigated using a vibrating sample magnetometer (VSM) of Meghnatis Daghigh Kavir Co. (Iran). X-ray photoelectron spectroscopy (XPS) was performed using a Thermo Scientific K-Alpha + XPS spectrometer (United States).

2.2 Preparation of Co_3O_4 nanoparticles

Magnetic Co_3O_4 nanoparticles were synthesized through the following reduction procedure: $CoCl_2.6H_2O$ (1.85 mmol; 0.440 g) was added in 15 mL of absolute EtOH while stirring at RT. Then, ethanol-dissolved pluronic P123 (0.2 g in 5 mL EtOH) was added to the aforementioned solution. After complete mixing, $NaBH_4$ (12.9 mmol; 0.487 g) was added, and the resulting combination was stirred for 10 min at RT. The obtained material was magnetically separated and then washed completely with warm EtOH and water to remove pluronic P123 and other impurities. The magnetic Co_3O_4 NPs were obtained after drying the product at 65°C for 5 h.

2.3 Synthesis of tetrahydrobenzo[b]pyrans using Co_3O_4 NPs

For this, dimedone (1.0 mmol), aldehyde (1.0 mmol), malononitrile (1.2 mmol), and a Co_3O_4 catalyst (0.015 g) were mixed in water (8 mL) while stirring at RT. The reaction progress was monitored by TLC. After completing the process, the catalyst was separated using an external magnetic field. Then, hot EtOH was added, and the resulting mixture was put in an ice bath to precipitate the pure product.

2.4 Procedure for the recovery of the Co_3O_4 NPs in the synthesis of tetrahydrobenzo[b]pyrans

For this, the reaction was performed as explained previously. After finishing the process, monitored by TLC, the catalyst was separated using a magnet. Then, the recovered catalyst was washed with EtOH and reused in the next run under the same conditions as the first run. These steps were repeated, and it was found that the

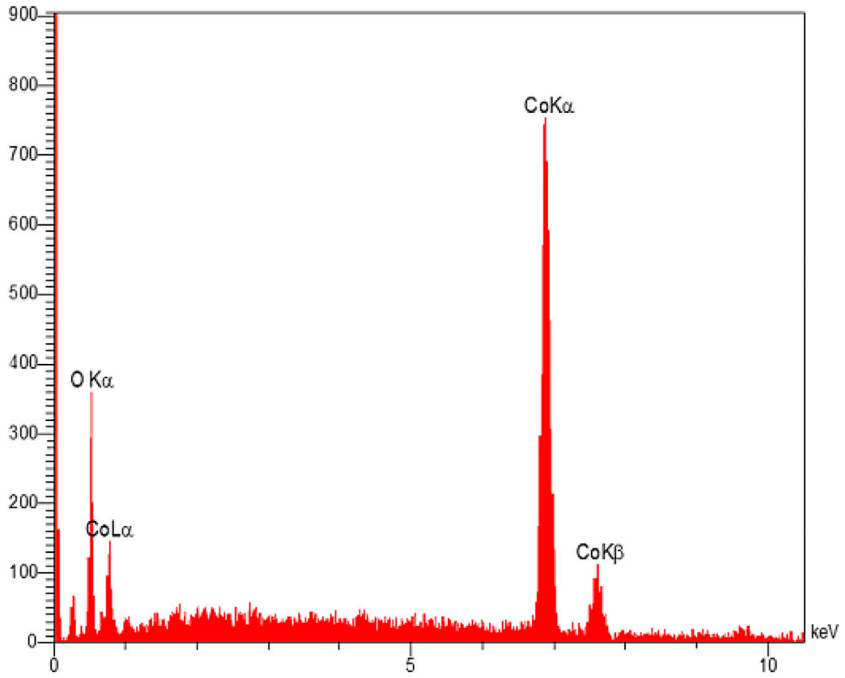


FIGURE 6
EDX image of the Co_3O_4 NPs.

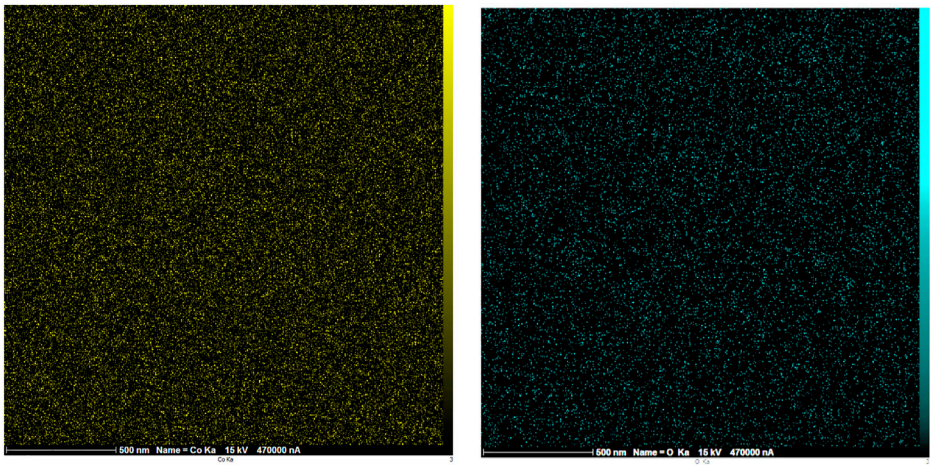


FIGURE 7
EDX mapping analysis of the Co_3O_4 NPs.

Co_3O_4 NPs can be recovered and reused several times with no significant decrease in their efficiency.

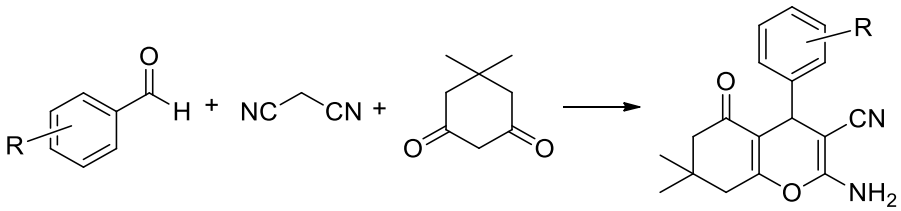
3 Result and discussion

The water- and air-stable magnetic Co_3O_4 nanoparticles were easily and rapidly prepared at RT through a novel reduction method in the presence of pluronic P123 as a stabilizer and $NaBH_4$ as a reducing agent (Scheme 1).

The Co_3O_4 NPs were characterized using FT-IR, PXRD, VSM, EDX, XPS, and SEM techniques. In the FT-IR spectrum (Figure 1) of Co_3O_4 NPs, the stretching vibration of the Co–O bond was observed at 619 cm^{-1}. The absorption peaks that appeared at 1,636 and 3,416 cm^{-1} are related to bending and stretching vibrations of OH, respectively. Furthermore, the band at 1,412 cm^{-1} is for the B–O bond, resulting from the hydrolysis of the borohydride ion (Medina et al., 2019).

The PXRD analysis shows nine peaks with low intensity at 2θ = 19, 32, 35, 37, 45, 56, 60, 65°, and 72° corresponding to the spinel

TABLE 1 Effect of catalyst loading, solvent, and temperature in the synthesis of tetrahydrobenzo[b]pyrans[a].



Entry	Catalyst (g)	Solvent	T (°C)	Yield (%)
1	-	H_2O	RT	-
2	0.01	H_2O	RT	68
3	0.015	H_2O	RT	96
4	0.02	H_2O	RT	95
5	0.015	EtOH	RT	63
6	0.015	THF	RT	42
7	0.015	CH_3CN	RT	30
8	0.015	Toluene	RT	15
9	0.015	H_2O	35	96
10	0.015	H_2O	50	96

[a]Conditions: dimedone (1.0 mmol), aldehyde (1.0 mmol), malononitrile (1.2 mmol), solvent (8 mL), 40 min.

TABLE 2 Synthesis of tetrahydrobenzo[b]pyrans in the presence of the Co_3O_4 catalyst.

Entry	Aldehyde	Dicarbonyl/coumarin	Time (min)	Yield (%)	M.P (°C)	
					Found	Reported
1	C_6H_5	Dimedone	40	96	231–234	231–233 Mohammadi et al. (2017)
2	4-MeC_6H_5	Dimedone	38	95	217–219	220–222 Elhamifar et al. (2018)
3	4-$MeOC_6H_5$	Dimedone	35	96	194–195	192–194 Seifi and Sheibani (2008)
4	3-HOC_6H_5	Dimedone	40	95	234–236	231–233 Hekmatshoar et al. (2008)
5	4-$NO_2C_6H_5$	Dimedone	20	94	175–177	177–178 Jin et al. (2004)
6	2-ClC_6H_5	Dimedone	37	95	210–212	213–215 Shirini et al. (2017)
7	3-BrC_6H_5	Dimedone	30	96	229–232	227–229 Salvi et al. (2011)
8	4-$NO_2C_6H_5$	4-Hydroxycoumarin	50	90	266–268	260–262 Farahi et al. (2017)

crystalline structure of magnetic Co_3O_4 NPs, which is in agreement with the previous literature (Figure 2) (He et al., 2004; Merino et al., 2012; Mujtaba et al., 2016; Hu et al., 2018).

The XPS analysis of cobalt oxide nanoparticles clearly shows the presence of Co and O elements (Figure 3). The most significant peaks related to O 1s, Co $2p_{3/2}$, and Co $2p_{1/2}$ appeared at 529.1, 780.1, and 795.8 eV, respectively. The energy difference between the Co $2p_{3/2}$ and Co $2p_{1/2}$ splitting is 15.7 eV, indicating the presence of Co^{2+} and Co^{3+} in the prepared material. These results are in good agreement with the previous reports and confirm the Co_3O_4 structure for the prepared material (Nwanya et al., 2017; Qiu et al., 2017; Zhang et al., 2017).

The morphology of the catalyst was studied by SEM. This analysis showed sponge-like spherical particles for the designed material (Figure 4). According to the SEM images, the average size of the designed Co_3O_4 NPs was about 36 nm.

In the next study, the magnetic properties of Co_3O_4 NPs were investigated using a vibrating sample magnetometer (VSM). Importantly, herein, two other methods were used to prepare magnetic Co_3O_4 NPs, and the magnetic properties of the resulting products were compared with those of our method (Figure 5). These methods were a) the milling process (Medina et al., 2019), b) EtOH/$NaBH_4$ without a stabilizer (our test), and c) ETOH/$NaBH_4$ in the presence of pluronic P123 as a stabilizer agent (our method). The VSM

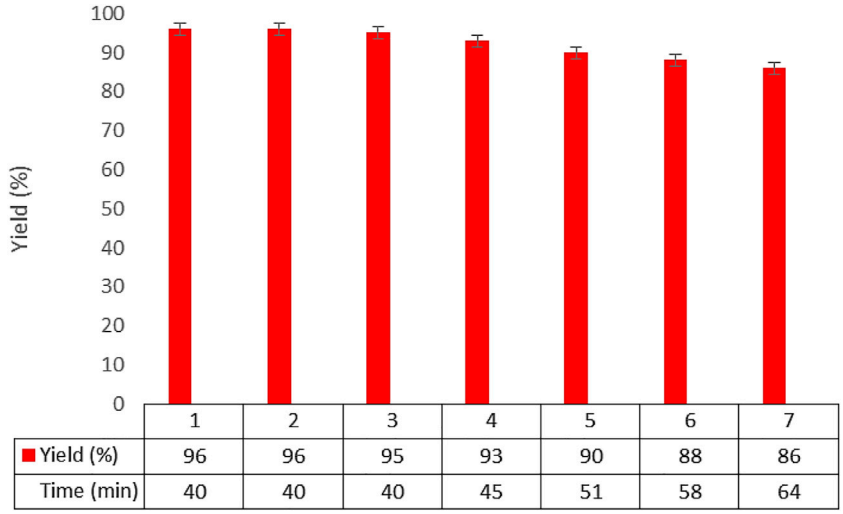


FIGURE 8
Recoverability and reusability of the Co_3O_4 catalyst.

TABLE 3 Comparison of the efficiency of Co_3O_4 nanoparticles with former catalysts[a].

Entry	Catalyst	Conditions	Yield (%)	Recovery times	[ref]
1	[Ch][OH]	H_2O, 80°C	92	5	Hu et al. (2014)
2	(H_2PO_4–SCMNPs)	Solvent-free, 80°C	88	4	Saadati-Moshtaghin and Zonoz (2017)
3	(NZF@HA–PRS)	H_2O, RT	88	4	Javid and Moeinpour (2018)
4	Eu@MNPs	EtOH, RT	94	5	Tamoradi et al. (2020)
5	Fe_3O_4@SiO_2–guanidine–PAA	H_2O, 70°C	96	5	Mohammadi and Sheibani (2019)
6	This work	H_2O, RT	96	6	—

[a][Ch][OH]: choline hydroxide-based ionic liquid; SCMNPs: silica-coated magnetic nanoparticles; NZF: $Ni0.5Zn0.5Fe_2O_4$; HA: hydroxyapatite; PRS: Preyssler heteropoly acid; Eu: europium; MNPs: magnetic nanoparticles; PAA: poly acrylic acid.

analysis showed the products with a magnetization of 28, 33, and 56 for the a, b, and c methods, respectively (Figure 5). This confirms the very good efficiency of our novel procedure to prepare Co_3O_4 NPs with high magnetic properties. This result is attributed to the key role of pluronic P123 as a surfactant in the stabilization of magnetic NPs during their preparation. It is also important to note that the prepared black Co_3O_4 NPs were easily separated using an external magnet (Figure 5, inset figure).

The EDX analysis was used to distinguish the elements in the structure of the Co_3O_4 material. This analysis showed the presence of O and Co in the Co_3O_4 structure (Figure 6). Moreover, the EDX mapping analysis also showed the uniform distribution of these elements in the material network (Figure 7).

After successful characterization, the Co_3O_4 NPs were used as an efficient catalyst in the synthesis of tetrahydrobenzo[b]pyrans. For this, the reaction between dimedone, benzaldehyde, and malononitrile was selected as a test model, and the effect of different parameters was studied (Table 1). In the absence of a catalyst, no product was found (Table 1, entry 1), while by adding the catalyst, the product yield was increased, and the best result was obtained using 0.015 g of Co_3O_4 NPs (Table 1, entries 2–4). Screening different solvents showed that a low yield in toluene and acetonitrile, a moderate yield in EtOH and THF, and the highest yield in water were obtained (Table 1, entries 3, 5–8). Increasing temperature from RT to 35°C and 50°C showed no significant change in the product yield (Table 1, entries 3, 9, 10). According to these results, 0.015 g of Co_3O_4, water solvent, and RT were chosen as optimum conditions (Table 1, entry 3).

With the optimal conditions in hand, the catalytic activity of Co_3O_4 was investigated for different aldehyde substrates to produce the tetrahydrobenzo[b]pyran derivatives. As shown, benzaldehyde (Table 2, entry 1), electron-donating containing aldehydes (Table 2, entries 2–4), and electron-withdrawing bearing aldehydes (Table 2, entry 5) are converted to the corresponding products in high yields at short times. Halogen-substituted aldehydes also delivered a high yield of the corresponding adducts (Table 2, entries 6, 7). In

addition, the reaction between 4-nitrobenzaldehyde, malononitrile, and coumarin in the presence of the Co_3O_4 nanocatalyst also gave a high yield of the corresponding product (Table 2, entry 8). These results confirm the high activity and efficiency of the Co_3O_4 catalyst for the preparation of a wide range of biologically active tetrahydrobenzo[b]pyrans.

The recoverability and reusability of the designed catalyst were investigated in the reaction model of benzaldehyde, dimedone, and malononitrile under optimal conditions. It was found that the Co_3O_4 nanocatalyst can be recovered and reused six times with no noticeable decrease in its activity (Figure 8).

Finally, the catalytic activity of the designed Co_3O_4 nanoparticles was compared with former heterogeneous catalysts in the synthesis of tetrahydrobenzo[b]pyrans (Table 3). It was found that the present catalyst has a high ability to synthesize desired products with higher efficiency and more recovery times than previous catalysts. These findings are attributed to the high surface area, excellent magnetic properties, and good stability of Co_3O_4 MNPs.

4 Conclusion

In this study, a novel and interesting method for the preparation of magnetic cobalt oxide (Co_3O_4) NPs was developed. These NPs were synthesized under green conditions at RT in a short time. The FT-IR, PXRD, SEM, VSM, XPS, and EDX analyses confirmed the good preparation, high stability, and good magnetic properties of Co_3O_4 NPs. These magnetic NPs were used as a powerful and efficient nanocatalyst for the synthesis of tetrahydrobenzo[b]pyrans. The desired products were obtained in water as an environmentally friendly solvent in a short time. The Co_3O_4 nanocatalyst was separated easily using an external magnet and recovered at least six times with no significant decrease in its activity. Due to the simplicity and eco-friendliness of the designed method, the preparation of other magnetic metal oxide NPs using this strategy is underway in our laboratory.

Data availability statement

The original contributions presented in the study are included in the article/supplementary material; further inquiries can be directed to the corresponding author.

Author contributions

HA: writing—original draft, investigation, resources, and formal analysis. DE: conceptualization, writing—review and editing, supervision, and visualization. All authors listed made a substantial, direct, and intellectual contribution to the work and approved it for publication.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Publisher's note

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