

A novel, effective, green and recyclable α -Fe₂O₃@MoS₂@Ni Magnetic nanocatalyst in preparation of a series of 1,2,4-triazolidine-3-thiones and spiro-triazole hybrids

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ABSTRACT

In current paper, a novel, green, efficient and recyclable magnetic nanocatalyst (α -Fe₂O₃@MoS₂@Ni) was prepared and characterized by spectroscopic and microscopic techniques (FT-IR, XRD, SEM, EDX, TEM and VSM). α -Fe₂O₃@MoS₂@Ni magnetic nanoparticles (MNPs) were utilized for preparation of 1,2,4-triazolidine-3-thiones and spiro-triazole hybrid series. In this method, a series of triazole derivatives prepared from the reaction between thiosemicarbazide or semicarbazide with diverse isatine derivatives or various arylaldehydes and ketones at room temperature in water as solvent with great yields and short reaction times. α -Fe₂O₃@MoS₂@Ni MNPs was simply removed from the reaction mixture and was reused for five times without any notable changes in its catalytic activity.

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Graphical Abstract

1. Introduction

Many biologically active and medicinal compounds have *N*-heterocycles in their chemical structure. These skeletons are one of the remarkable groups in organic and medicinal chemistry. Triazoles are one of the five-membered nitrogen-containing heterocycles that have two carbon atoms and three nitrogen atoms in their structure¹⁻⁷. Most of the compounds having triazole skeleton show significant biological properties such as: anti-bacterial, anti-microbial, anti-tumor, anti-inflammatory, anti-fungal, antimalarial, anti-cancer, anti-tumor, anti-HIV, etc.⁸⁻¹⁶ Various derivatives of triazole rings are also found in multitudes of natural compounds. Several examples of the biological activities of triazole derivatives are

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reported¹⁷⁻²⁷. Recently, various catalysts containing the triazole ring have been reported and used in the preparation of organic compounds (**Fig. 1**)²⁸⁻³⁰. Thus, considering the importance of triazoles, diverse methods have been reported for their synthesis. Various reaction conditions such as: γ -Fe₂O₃@FAp@Cr³¹ and Co³² in ethanol, Fe₃O₄@SiO₂@Tannic acid³³ nanoparticles in CHCl₃, amino glucose-functionalized silica-coated NiFe₂O₄ MNPs³⁴ in ethanol, [C₁₆MPy]AlCl₃Br³⁵ in water are some of those. Previously reported methods for synthesis of triazole derivatives have some disadvantages such as tough reaction conditions, intricate synthetic pathways, harsh separation of the catalyst from the reaction mixture, as well as long reaction times with low yield. Hence, simpler and more efficient methods are still in demand. Consequently, we decided to develop an effective method for the synthesis of some of 1,2,4-triazolidine-3-thiones and spiro-triazole hybrid series by using a novel, green and recyclable α -Fe₂O₃@MoS₂@Ni nanocatalyst. Facile removal of the nano particles from the reaction mixture, short reaction time, excellent yields and reusability of the nanocatalyst could be mentioned as some of the introduced method's advantages.

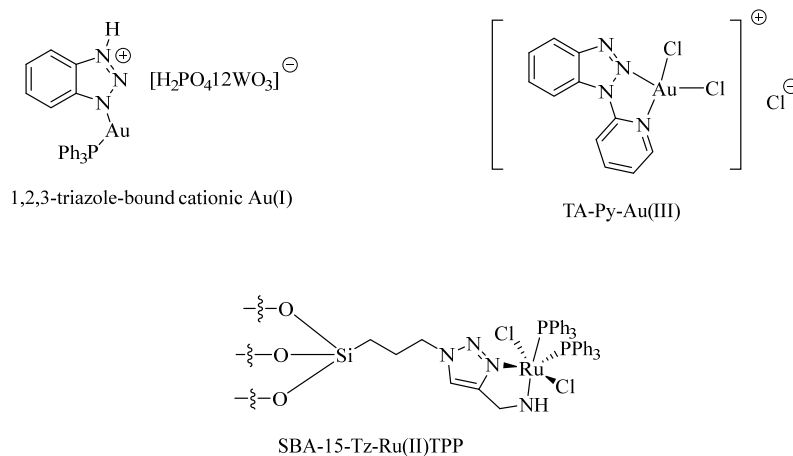


Fig. 1. Some catalysts containing the triazole ring²⁸⁻³⁰

2. Results and discussion

Preparation and characterization of the catalyst

The α -Fe₂O₃@MoS₂ was prepared corresponding to the previous reports³⁵⁻³⁸. Then, the α -Fe₂O₃@MoS₂ in ethanol (suspension A) reacted with NiCl₂.6H₂O in 4% water/NH₃ solution (suspension B) at 80 °C for 1 hour. The resulting α -Fe₂O₃@MoS₂@Ni NPs was collected and purified by washing three times with deionized water (DW). The structure of the α -Fe₂O₃@MoS₂@Ni magnetic nanocatalyst was characterized by spectroscopic and microscopic techniques (FT-IR, XRD, SEM, EDX, TEM and VSM).

XRD analysis

The XRD analysis of α -Fe₂O₃@MoS₂@Ni magnetic nanoparticle is shown in **Fig. 2**.

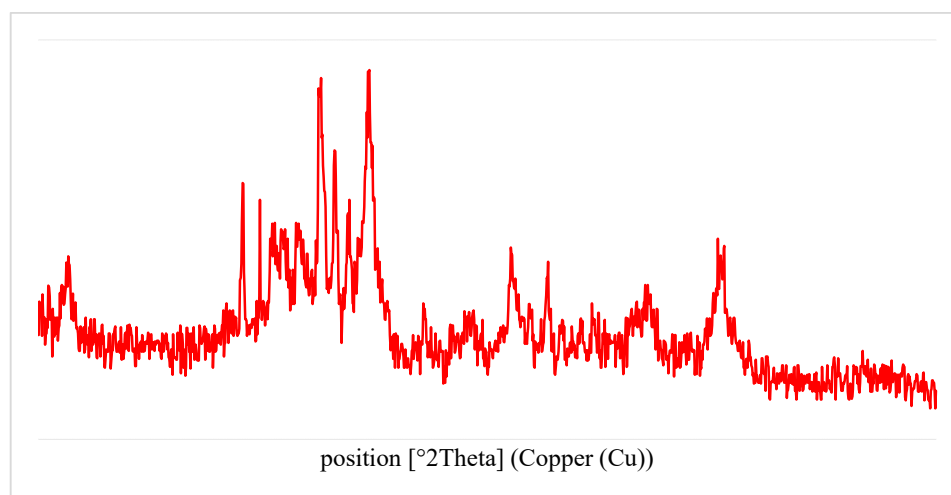


Fig. 2. The XRD image of α -Fe₂O₃@MoS₂@Ni. Powder X-ray diffraction (XRD) pattern was accomplished on a KEFA Analytical XPERT-PRO diffractometer with Cu-K α source ($\lambda=1.54060$ Å) in a voltage of 40 kV and a current of 40 mA at room temperature over 2θ range 2–80° at a scan rate of 0.1° 2 θ /s

The XRD analysis of $\alpha\text{-Fe}_2\text{O}_3@\text{MoS}_2@\text{Ni}$ shows diffraction peaks at around $2\theta = 14.7^\circ, 33.4^\circ, 36.8^\circ$ and 59.7° which are related to the MoS_2 (JCPDS card No. 37-1492). Diffraction peaks at around $2\theta = 32.5^\circ, 35.8^\circ, 40.3^\circ$, and 49.6° are also assigned to the $\alpha\text{-Fe}_2\text{O}_3$ (JCPDS File No. 79-0007). The peaks at $2\theta = 32.7^\circ, 35.3^\circ$ and 39.4° are related to the FeS phase (JCPDS card No. 37-0477). The peaks at $2\theta = 45.2, 47.3$, and 74.7 are related to nickel species in the nanomaterial system (JCPDS card No. 65-0380). The average size of the nanoparticles was calculated to be 60 nm using the Scherrer equation.

SEM image of $\alpha\text{-Fe}_2\text{O}_3@\text{MoS}_2@\text{Ni}$ MNPs

The morphology and particle size of the $\alpha\text{-Fe}_2\text{O}_3@\text{MoS}_2@\text{Ni}$ MNPs were checked by Scanning Electron Microscope technique (**Fig. 3**). According to the SEM images of $\alpha\text{-Fe}_2\text{O}_3@\text{MoS}_2@\text{Ni}$ magnetic nanocatalyst spherical morphology is verified for the nanocatalyst particles. The obtained average size of the synthesized nanoparticles is about 65 nm.

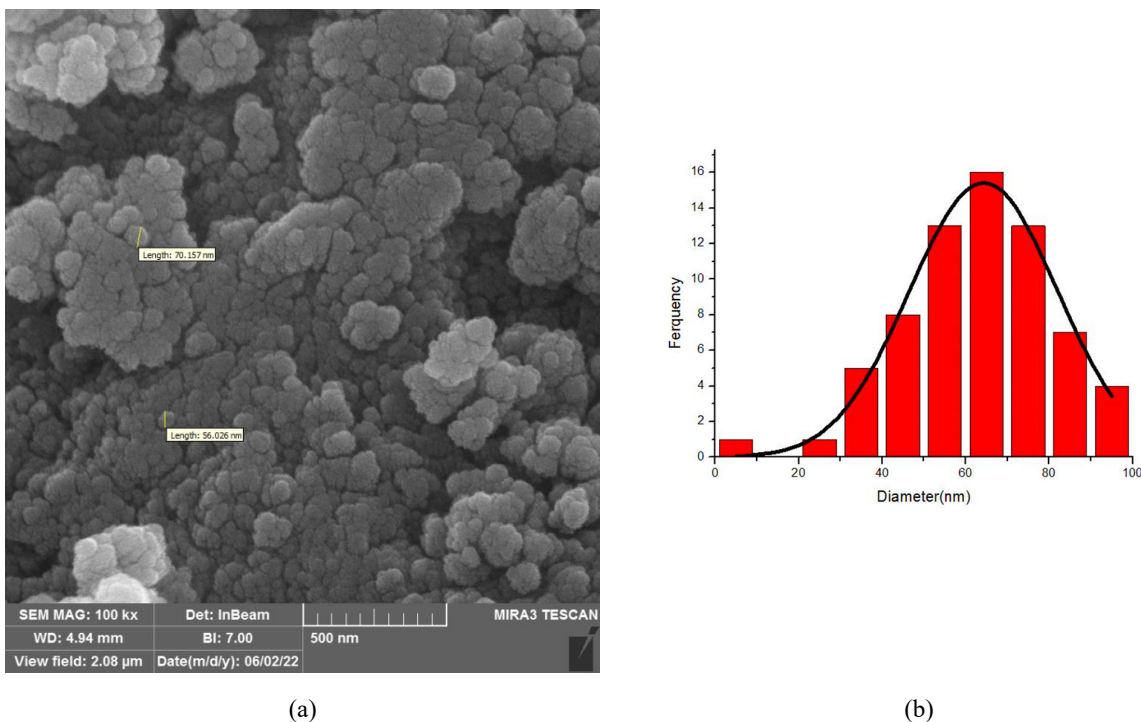


Fig. 3. (a) The SEM micrograph of the $\alpha\text{-Fe}_2\text{O}_3@\text{MoS}_2@\text{Ni}$ nanoparticles (b) The histogram of SEM micrograph of the $\alpha\text{-Fe}_2\text{O}_3@\text{MoS}_2@\text{Ni}$ nanoparticles. SEM analyses were recorded on Oxford Instruments EDS Microanalysis X-MAX-80; model: TeScan-Mira III. instrument at accelerating voltage of 15 kV with an Au layer coating on carbon support.

EDX analysis

The results of EDX analysis of $\alpha\text{-Fe}_2\text{O}_3@\text{MoS}_2@\text{Ni}$ nanocatalyst verified the existence of Iron, Oxygen, Sulfur, Molybdenum and Nickel atoms in the nanoparticles structure (**Fig. 4**).

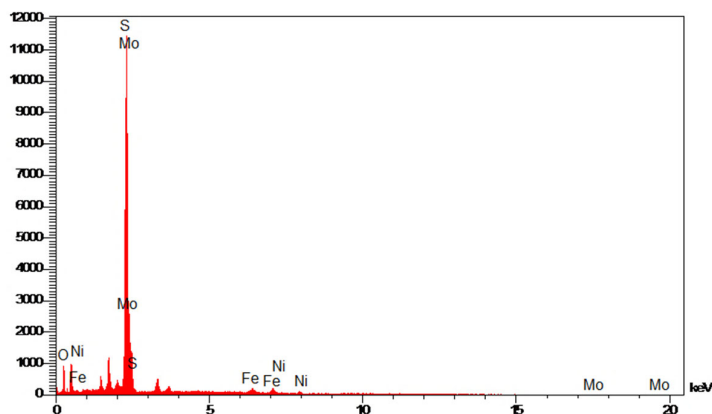


Figure 4. The EDX image of $\alpha\text{-Fe}_2\text{O}_3@\text{MoS}_2@\text{Ni}$. Energy-dispersive X-ray spectroscopy was checked on Oxford Instruments EDS Microanalysis X-MAX-80; model: TeScan-Mira III. instrument at accelerating voltage of 15 kV with an Au layer coating on carbon support.

FT-IR spectrum

In the FT-IR spectra of $\alpha\text{-Fe}_2\text{O}_3@\text{MoS}_2@\text{Ni}$ NPs the band at 566 cm^{-1} belongs to the stretching vibration of Fe-O. The stretching vibration of Mo-O band is appeared at 1043 cm^{-1} . The broad band at 3437 cm^{-1} is related to the stretching vibrations of the O-H groups and adsorbed water (**Fig. 5**).

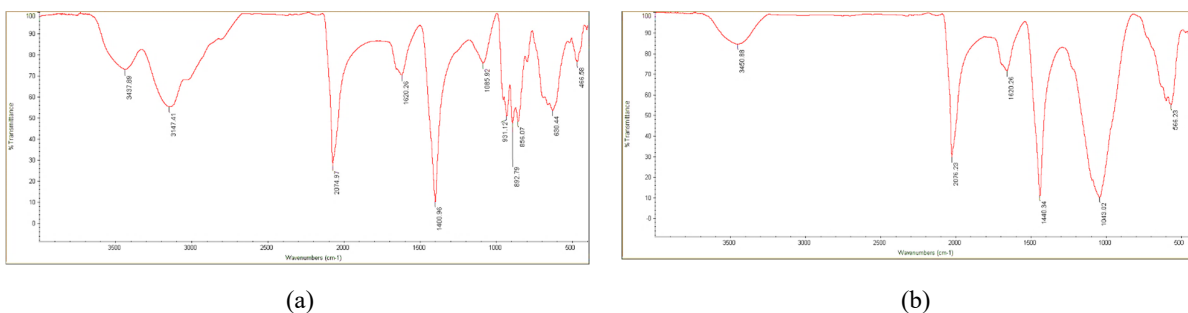


Fig. 5. FT-IR spectra of (a) MoS_2 and (b) $\alpha\text{-Fe}_2\text{O}_3@\text{MoS}_2@\text{Ni}$. The FT-IR spectrum of the samples were obtained on a α -Bruker spectrometer by KBr pills. The spectrum was investigated in the range of $400\text{--}4000\text{ cm}^{-1}$ with a resolution of 4 cm^{-1} at room temperature.

VSM image of $\alpha\text{-Fe}_2\text{O}_3@\text{MoS}_2@\text{Ni}$ MNPs

The VSM curve of the $\alpha\text{-Fe}_2\text{O}_3@\text{MoS}_2@\text{Ni}$ magnetic nanoparticles was recorded by a vibrating sample magnetometer at 25°C (**Fig. 6**). The results cleared that the $\alpha\text{-Fe}_2\text{O}_3@\text{MoS}_2@\text{Ni}$ nanocatalyst could have superparamagnetic behavior at room temperature. The magnetic properties of nanoparticles led to the easy removal and then recyclability of the catalyst by applying an external magnet.

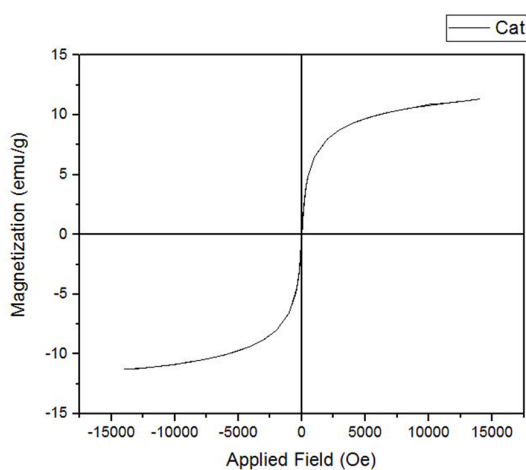


Fig. 6. The VSM curve of the $\alpha\text{-Fe}_2\text{O}_3@\text{MoS}_2@\text{Ni}$. The magnetic measurement was checked using a BHV-55 vibrating sample magnetometer at room temperature gradient force Magnetometer (VSM/ AGFM, MDK Co, Ltd).

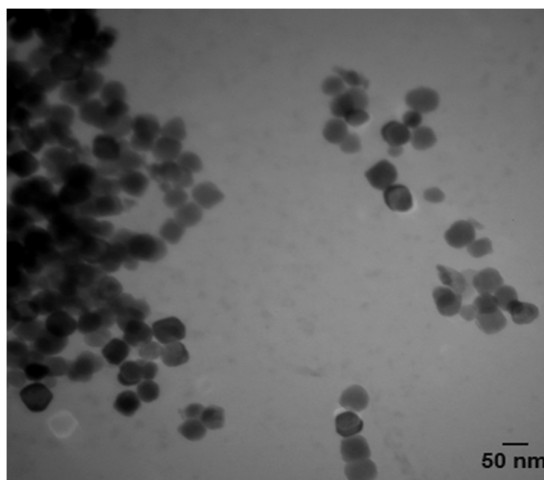
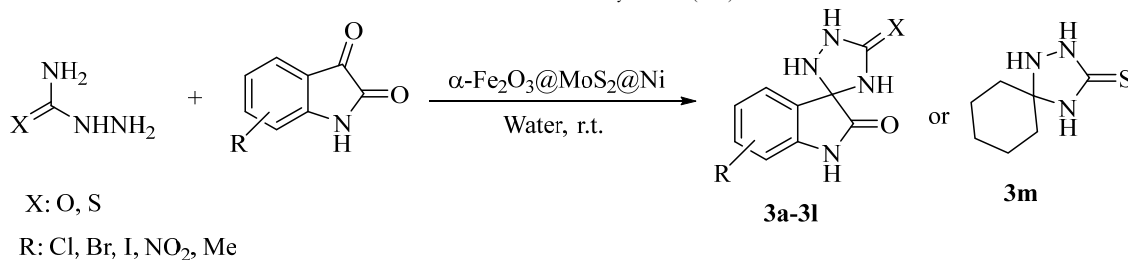


Fig. 7. TEM image of the $\alpha\text{-Fe}_2\text{O}_3@\text{MoS}_2@\text{Ni}$. Transmission electron microscopy (TEM) measurements were recorded on a Zeiss - EM10C-100 KV microscope, utilized with 100 kV with a carbon coated grid Cu Mesh 300.

TEM image of $\alpha\text{-Fe}_2\text{O}_3@\text{MoS}_2@\text{Ni}$ MNPs

The morphology and size of the $\alpha\text{-Fe}_2\text{O}_3@\text{MoS}_2@\text{Ni}$ magnetic nanoparticles were obtained via the TEM analysis (**Fig. 7**). According to the TEM spectra, the size of the $\alpha\text{-Fe}_2\text{O}_3@\text{MoS}_2@\text{Ni}$ nanoparticles was estimated to be about 60-70 nm.

After the synthesis and identification of the $\alpha\text{-Fe}_2\text{O}_3@\text{MoS}_2@\text{Ni}$ magnetic nanocatalyst by spectroscopic and microscopic techniques, we investigated its catalytic activity in the preparation of some spiro-triazole hybrids (**Scheme 1**). In order to optimize the reaction conditions, thiosmicarbazide (**1**) and indoline-2,3-dione (**2**) using $\alpha\text{-Fe}_2\text{O}_3@\text{MoS}_2@\text{Ni}$ MNPs in different conditions such as: using various solvents at different temperatures as a model reaction, were checked. (**Table 1**).



Scheme 1. Synthesis of the spiro-triazole hybrid series using $\alpha\text{-Fe}_2\text{O}_3\text{@MoS}_2\text{@Ni}$ MNPs.

Investigating the effect of diverse catalysts and various solvents on the reaction time and yield was evaluated. The obtained results demonstrated that the reaction in water at room temperature in the presence of $\alpha\text{-Fe}_2\text{O}_3\text{@MoS}_2\text{@Ni}$ MNPs leads to the target product **3a** in 5 min and 95% yield (**Table 1, Entry 8**). This method displayed that the reaction in the presence of $\alpha\text{-Fe}_2\text{O}_3\text{@MoS}_2\text{@Ni}$ magnetic nanocatalyst produces acceptable results.

Table 1. Synthesis of **3a** using $\alpha\text{-Fe}_2\text{O}_3\text{@MoS}_2\text{@Ni}$ MNPs in diverse solvents and temperatures

Entry	Solvent	Temperature (°C)	Time (min)	Yield (%) ^{a,b}
1	EtOH	25	5	90
2	MeOH	25	5	92
3	CH ₃ CN	25	15	85
4	CHCl ₃	25	15	88
5	THF	25	20	trace
6	Toluene	25	20	trace
7	H ₂ O/EtOH	25	5	93
8	H ₂ O	25	5	95
9	H ₂ O	50	5	95
10	H ₂ O	100	5	95

^aisolated yield. ^bReaction conditions: semicarbazide 1 (1 mmol), indoline-2,3-dione **2a** (1 mmol), solvent (5 mL), catalyst (5 mol%).

The current method is compared with other methods reported in scientific references. This study showed that the method reported in this research has a better result.

Table 2. Synthesis of **3a** using reported methods and current method.

Entry	Catalyst	Solvent	Temperature (°C)	Time (min)	Yield (%) ^{a,b}	Reference
1	[2-HMPyBSA] HSO ₄	Water	r. t.	7	89	41
2	Gly-NO ₃ ⁻	Water	80	240	88	39
3	-	PEG-400	80	9	93	38
4	$\alpha\text{-Fe}_2\text{O}_3\text{@MoS}_2\text{@Ni}$	Water	r. t.	5	95	Current method

^aisolated yield. ^bReaction conditions: semicarbazide 1 (1 mmol), indoline-2,3-dione **2a** (1 mmol), solvent (5 mL), room temperature.

The effect of the amount of nanocatalyst used on the progress of the model reaction was investigated in the vicinity of different amounts of the catalyst, the results of which are given in **Table 3**. (**Table 3, entry 2**).

Table 3. Investigating the effect of the amount of catalyst on the efficiency and synthesis time of compound **3a** in water solvent and at room temperature.

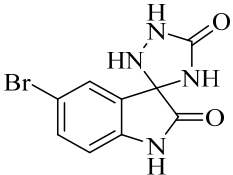
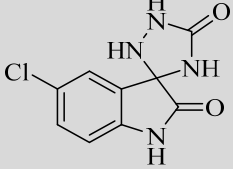
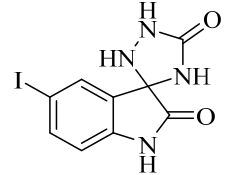
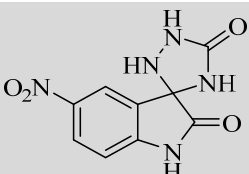
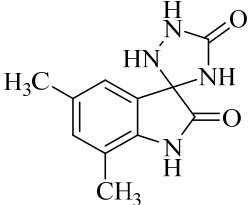
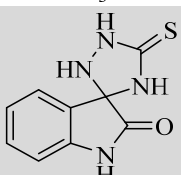
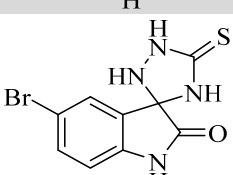
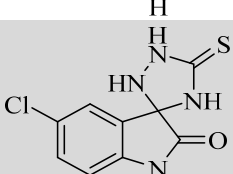
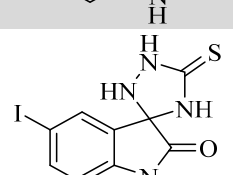
Entry	amount of catalyst (mol%)	Time (min)	Yield (%) ^{a,b}
1	2	10	92
2	5	5	95
3	10	5	95

^aIsolated yield. ^bReaction conditions: semicarbazide 1 (1 mmol), indoline-2,3-dione **2a** (1 mmol), solvent (5 mL), room temperature, catalyst 5 mol%.

The current method was used to prepare a series of diverse spiro-triazole hybrids under the optimum reaction conditions and the results are demonstrated in **Table 4**.

Table 4. Synthesis of spiro-triazole hybrids (**3a-m**) via $\alpha\text{-Fe}_2\text{O}_3\text{@MoS}_2\text{@Ni}$ MNPs under optimized conditions.

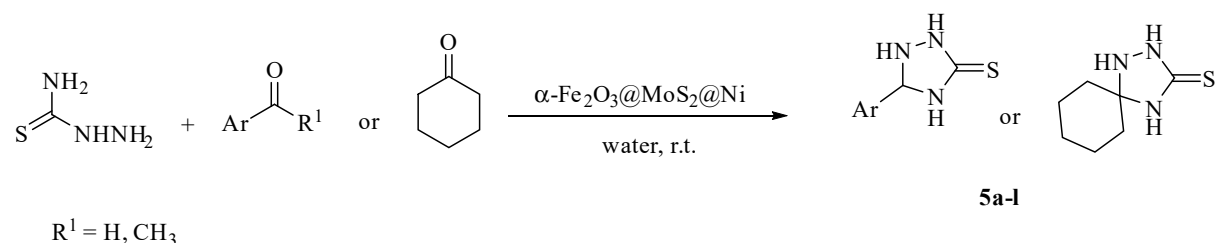
Entry	product	structure	Time (min)	M.P (Observed)	M.P (reported)	Yield (%) ^{a,b}
1	3a		5	254-256	255-257 ³⁹	95

2	3b		10	266-268	265-267 ³⁹	93
3	3c		12	290-292	289-290 ³⁹	90
4	3d		15	277-279	277-278 ³⁹	91
5	3e		12	> 300	> 300 ³⁹	95
6	3f		15	290-292	291-293 ³⁹	94
7	3g		5	251-252	250-252 ³⁹	92
8	3h		15	267-269	268-270 ³⁹	94
9	3i		15	280-282	280-282 ³⁹	95
10	3j		15	265-267	266-268 ³⁹	90

11	3k	10	> 300	>300 ³⁹	95
12	3l	15	280-282	279-280 ³⁹	90
13	3m	5	155-157	156-158 ⁴⁰	95

^aIsolated yield. ^bReaction conditions: semicarbazide or thiosemicarbazide (1 mmol), Aldehyde or Ketone (1 mmol), solvent (5 mL), room temperature, catalyst 5 mol%.

In the following, from the reaction between thiosemicarbazide and ketones or arylaldehyde derivatives in water in the presence of the $\alpha\text{-Fe}_2\text{O}_3\text{@MoS}_2\text{@Ni}$ MNPs were reacted at room temperature (Scheme 2) and their result led to the production of products **5a-l** in reasonable yields (Table 5).



Scheme 2. Synthesis of a series of 1,2,4-triazolidine-3-thiones using $\alpha\text{-Fe}_2\text{O}_3\text{@MoS}_2\text{@Ni}$ MNPs.

Fig. 8. shows the recyclability of the $\alpha\text{-Fe}_2\text{O}_3\text{@MoS}_2\text{@Ni}$ MNPs in the preparation of model product **3a**. After the completion of each reaction, the magnetic nanocatalyst was removed from the reaction mixture using an external magnet bar, then washed with warm water, dried at 100°C and reused in the subsequent run. This study demonstrated that the catalytic activity of the $\alpha\text{-Fe}_2\text{O}_3\text{@MoS}_2\text{@Ni}$ MNPs preserved after five repeated runs.

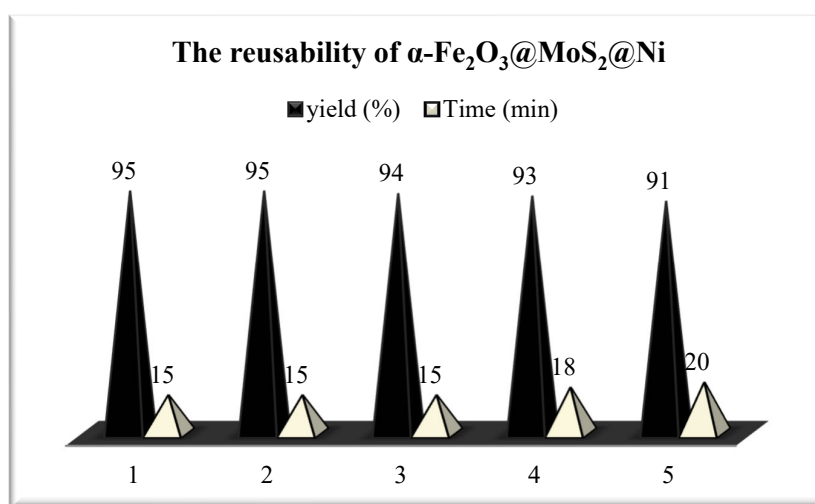
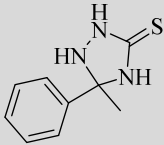
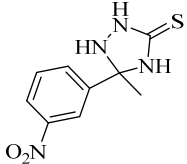
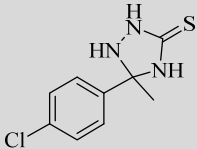
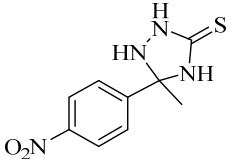
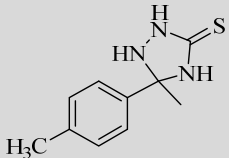
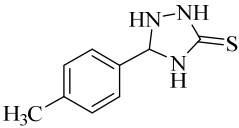
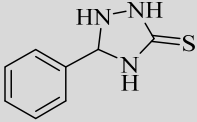
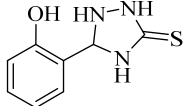
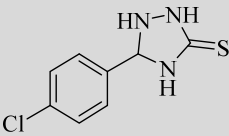
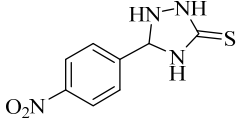
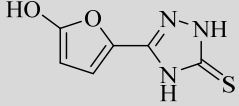
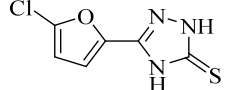


Fig. 8. The recyclability of $\alpha\text{-Fe}_2\text{O}_3\text{@MoS}_2\text{@Ni}$ for the synthesis of product **3a**. ^aReaction conditions: semicarbazide 1 (1 mmol), indoline-2,3-dione **2a** (1 mmol), solvent (5 mL), room temperature, catalyst 5 mol%.

Table 5. Synthesis of a series of 1,2,4-triazolidine-3-thiones (**5a-l**) using $\alpha\text{-Fe}_2\text{O}_3@\text{MoS}_2@\text{Ni}$ MNPs.

Entry	product	structure	Time (min)	M.P (Observed)	M.P (reported)	Yield (%) ^{a, b}
1	5a		5	216-218	215-218 ⁴⁰	94
2	5b		4	199-201	200-202 ⁴⁰	95
3	5c		4	204-206	205-206 ⁴⁰	93
4	5d		2	266-268	266-268 ⁴⁰	95
5	5e		5	176-178	175-177 ⁴⁰	92
6	5f		5	175-177	174-176 ⁴⁰	94
7	5g		5	151-152	152-153 ⁴⁰	95
8	5h		5	215-217	216-218 ⁴⁰	91
9	5i		3	206-208	206-208 ⁴⁰	94
10	5j		2	212-214	213-214 ⁴⁰	95
11	5k		15	126-129	new	94
12	5l		15	155-158	new	92

^aIsolated yield. ^bReaction conditions: thiosemicarbazide (1 mmol), Aldehyde or Ketone (1 mmol), solvent (5 mL), room temperature, catalyst 5 mol%.

3. Conclusion

In this research, $\alpha\text{-Fe}_2\text{O}_3@\text{MoS}_2@\text{Ni}$ as a novel, effective, eco-friendly, recyclable and inexpensive magnetic nanocatalyst was successfully prepared and used for the synthesis of a series of 1,2,4-triazolidine-3-thiones and spiro-triazole hybrids. The obvious advantages of this method include high reaction yield, short reaction time, easily purification of products without the need for chromatographic separation., facile separation and reuse of the catalyst for several times without remarkable changes in its catalytic activity.

Acknowledgments

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Conflict of Interest

There are no relevant financial or non-financial competing interests to report.

4. Experimental

Chemicals and reagents

In this research, all of chemicals were purchased from Merck and Fluka

Characterization techniques

Melting points were obtained on a Büchi B-545 apparatus in open capillary tubes. FT-IR spectra were considered on a α -Bruker spectrometer. ^1H NMR spectra were determined on a 300 MHz Bruker DRX-300 in DMSO- d_6 as solvent and TMS as internal standard. ^{13}C NMR spectra were done on a 75 MHz Bruker DRX-75 in DMSO- d_6 as solvent. XRD were investigated on a KEFA Analytical XPERT-PRO. Scanning Electron Microscope (SEM) were recorded on a model: VP 1450, company: LEO-Germany. Elemental analysis (EDX) was checked on Oxford Instruments EDS Microanalysis X-MAX-80; model: TeScan-Mira III. TEM measurements were done on a Zeiss-EM10C-100 KV instrument. VSM spectrum was checked by a BHV-55 vibrating sample magnetometer at room temperature. TLC was considered by ethyl acetate: n-hexane (1:1) on TLC Silica gel 60 F₂₅₄.

The catalyst preparation

preparation of $\alpha\text{-Fe}_2\text{O}_3@\text{MoS}_2@\text{Ni}$ MNPs

$\alpha\text{-Fe}_2\text{O}_3@\text{MoS}_2$ nanocatalyst was synthesized corresponding to the papers³⁶⁻³⁸. 5.0 mg of $\alpha\text{-Fe}_2\text{O}_3@\text{MoS}_2$ was stirred in 3 ml of EtOH via ultrasonic to give suspension 1, In continuation, 20 mmol $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ (4.7 mg) was dissolved in 5 ml DW and then 4% diluted NH_3 was dropped into the NiCl_2 solution until the turbid solution be clear (solution 2). Eventually, solution 2 was blended with suspension 1, and the final suspension was refluxed for 1 hour. The resulting product was separated using a foreign magnet, washed with warm Water repeatedly, and dried at 100 °C to give $\alpha\text{-Fe}_2\text{O}_3@\text{MoS}_2@\text{Ni}$ as a dark brown solid.

General procedure for the synthesis of 1,2,4- triazolidine-3-thiones

A mixture of semicarbazide or thiosemicarbazide (1 mmol), indoline-2,3-dione derivatives (or diverse arylaldehyde and various ketones) (1 mmol) and $\alpha\text{-Fe}_2\text{O}_3@\text{MoS}_2@\text{Ni}$ (5% mmol) were stirred in water at room temperature and the progress of the reaction was obtained using TLC (ethyl acetate: n-hexane 1: 1). Finally, The obtained product was purified by recrystallization with ethanol and product 5'-thioxospiro[indoline-3,3'-[1,2,4]triazolidin]-2-one was produced with 95 % yield. $\alpha\text{-Fe}_2\text{O}_3@\text{MoS}_2@\text{Ni}$ MNPs were recovered, washed, dried and reused in the next run under same reaction conditions. (Table 4 and Table 5). The melting point of all products was confirmed by comparing their melting temperature with the reported value and spectroscopic data of the selected already reported compounds were investigated using comparing their spectroscopic data reported³⁹⁻⁴² (Table 4). Two new derivatives of 1,2,4-triazolidin-3-thiones were synthesized by furan aldehyde derivatives and thiosemicarbazide under the same mentioned conditions. The structure of product **5k-5l** checked using FT-IR, ^1H NMR and ^{13}C NMR.

Physical and Spectroscopic data of the selected already reported and novel compounds:

spiro[indoline-3,3'-[1,2,4]triazolidine]-2,5'-dione (3a): Yield 95%, Yellow solid; M. p. 254-256 °C. FT-IR (KBr), ν , cm^{-1} : 3266, 3122 (N-H), 3040, 2920, 2869 (C-H), 1703, 1691 (C=O), 1608, 1520, 1543 (C=C), 815, 785, 721.

5-chlorospiro[indoline-3,3'-[1,2,4]triazolidine]-2,5'-dione (3c): Yield 90%, Yellow solid; M. p. 290-292 °C. FT-IR (KBr), ν , cm^{-1} : 3265 (N-H), 3063, 2917 (C-H), 1705, 1691 (C=O), 1589, 1529, 1457 (C=C), 1125 (C-Cl), 861, 752, 648.

5,7-dimethyl-5'-thioxospiro[indoline-3,3'-[1,2,4]triazolidin]-2-one (3l): Yield 90%, Brown solid; M. p. 280-282 °C. FT-IR (KBr), ν , cm^{-1} : 3256, 3183, 3110 (N-H), 3050, 3924, 2866 (C-H), 1702 (C=O), 1672 (C=S) 1592, 1532, 1482 (C=C),

1392 (CH₃), 877, 819, 768.

5-methyl-5-(4-nitrophenyl)-1,2,4-triazolidine-3-thione (5d): Yield 95%, Yellow solid; M. p. 199-201 °C. FT-IR (KBr), ν , cm⁻¹: 3297, 3188, 3111 (N-H), 1632 (C=S), 1595, 1504, 1441 (C=C), 1526, 1341 (NO₂), 1380 (CH₃), 839, 756, 718.

5-phenyl-1,2,4-triazolidine-3-thione (5g): Yield 95%, White solid; M. p. 151-152 °C. FT-IR (KBr), ν , cm⁻¹: 3396, 3278 (N-H), 3049, 3947 (C-H), 1636 (C=S), 1598, 1535, 1500 (C=C), 836, 750, 683.

5-(4-nitrophenyl)-1,2,4-triazolidine-3-thione (5j): Yield 95%, Yellow solid; M. p. 212-214 °C. FT-IR (KBr), ν , cm⁻¹: 3427, 3241, 3151 (N-H), 3051 (C-H), 1647 (C=S), 1602 (C=C), 1512, 1361 (NO₂), 825, 769, 684.

5-(5-hydroxyfuran-2-yl)-2,4-dihydro-3H-1,2,4-triazole-3-thione (5k): Yield 94%, Cream solid; M. p. 126-129 °C. FT-IR (KBr), ν , cm⁻¹: 3264, 3133 (N-H or O-H), 3058, 2873 (C-H), 1685 (C=S), 1600, 1544, 1493 (C=C and C=N), 1252, 1077 (C-O-C). ¹H NMR (300 MHz, DMSO-d₆), δ , ppm: 7.46 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.7 Hz, 1H), 8.04 (s, 1H, OH), 8.09 (s, 1H, NH), 8.26, (s, 1H, NH). ¹³C NMR spectrum (75 MHz, DMSO-d₆), δ , ppm: 161.9, 141.3, 134.7, 133.7, 129.4, 129.2.

5-(5-chlorofuran-2-yl)-2,4-dihydro-3H-1,2,4-triazole-3-thione (5l): Yield 92%, Cream solid; M. p. 155-158 °C. FT-IR (KBr), ν , cm⁻¹: 3425 (N-H), 3063, 2918 (C-H), 1687 (C=S), 1608, 1588, 1493 (C=C and C=N), 1252, 1023 (C-O-C), 1120 (C-Cl). ¹H NMR (300 MHz, DMSO-d₆), δ , ppm: 7.73 (d, *J* = 6.8 Hz, 1H), 7.97 (d, *J* = 6.6 Hz, 1H), 8.57 (s, 1H, NH), 9.85, (s, 1H, NH). ¹³C NMR spectrum (75 MHz, DMSO-d₆), δ , ppm: 160.1, 146.1, 139.5, 132.6, 130.6, 130.2.

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