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Magnetically recyclable sepiolite/iron oxide/cupric oxide nanocomposite as a novel catalyst for the synthesis of *S*-aryl dithiocarbamates by C—S bond formation

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Abstract

A convenient and efficient procedure is described for the synthesis of *S*-aryl dithiocarbamates by C–S bond formation through the coupling reaction of three components between secondary amines, carbon disulfide, and aryl iodides using magnetically separable and reusable sepiolite/iron oxide/cupric oxide (SEP/Fe₃O₄/CuO) nanocomposite as a heterogeneous catalyst. The results show that (SEP/Fe₃O₄/CuO) nanocomposite has good activity, and could be easily separated from the reaction mixture using an external magnet. The high efficiency of the nanocomposite was related to the temperature of 100° C and dimethylformamide (DMF) as a solvent. The structure, morphology, and crystalline phases of the prepared (SEP/Fe₃O₄/CuO) nanocomposite were characterized by Fourier transform infrared spectroscopy (FT-IR), vibrating-sample magnetometer (VSM), scanning electron microscopy (SEM), inductively coupled plasma (ICP), and X-ray powder diffraction (XRD).

K E Y W O R D S

carbon disulfide, cupric oxide, heterogeneous catalyst, S-aryl dithiocarbamates, sepiolite

1 | INTRODUCTION

Carbon-heteroatom cross-coupling reactions play a vital role in synthesizing organic compounds^[1,2] and they are a crucial step in designing the synthesis of industrially and biologically active materials. These reactions were used in synthesizing therapeutic medicines for diabetes, inflammation, HIV, and cancer.^[3–5] Methods used for the C–S bond-forming are vital tools in synthetic chemistry because of the frequent occurrence of these structural units in biologically active molecules.^[6–7] Their importance is due to the broad utilizations of organo-sulfur compounds in diverse sciences.^[8] So, the formation of carbon–sulfur bonds is an essential part in the preparation of numerous biological, pharmaceutical, and chemical molecules.^[9] Forming a C–S bond is a fundamental approach to introduce sulfur into organic compounds.

The bond formation between carbon and sulfur is relatively problematic due to the parallel oxidative S—S bond creation and consequently deactivation of metal-based catalysts by sulfur-containing compounds. A wide range of transition metals, including Cu,^[10–11] Pd,^[12] Ni,^[13] Co,^[14] and Fe^[15] catalysts, with suitable ligands, are all well explored for C—S bond-forming.

S-aryl dithiocarbamates, due to their interesting chemistry and wide range of utilities, are vital structural forms occurring in numerous natural products,^[16] agrochemicals and pharmaceuticals.^[17] They have many potential applications, for example, as linkers in solid phase organic synthesis,^[18] agrochemicals,^[19] as versatile synthetic intermediates,^[20] biologically active compounds,^[16] protecting groups in peptide synthesis,^[21] and in the synthesis of ionic liquids.^[22] The most common method in synthesizing the dithiocarbamates is the reaction of amines with isothiocyanates or thiophosgene,^[23] 2

which are not environmentally acceptable.^[24] Most of the protocols, however, suffer from drawbacks such as harsh reaction conditions, high temperature, prolonged reaction time, use of homogeneous catalyst, and rapid loss of catalytic activity. Although the acceptable yield for the synthesis of dithiocarbamates has been reported in most protocols, the improvement of protocols for the synthesis of these compounds, which are cheap, practical, and environmentally benign, is highly desirable. Therefore, developing low-cost, practical, and environmentally benign protocols for the synthesis of dithiocarbamates is highly desirable. The present paper reports a one-pot multicomponent condensation of amines, carbon disulfide, and aryl halides for the synthesis of S-aryl dithiocarbamates by C-S bond formation with a magnetically recyclable sepiolite/iron oxide/cupric oxide (SEP/Fe₃O₄/CuO) nanocomposite (Scheme 1).

Basically, the catalyst is considered as a chemical compound able to exert a directing and accelerating effect on the progress of a reaction that is thermodynamically possible. When the phase catalyst forms a separate phase from the reaction phase, it is called a "heterogeneous catalyst", and in the case of a catalyst soluble in the reaction medium, it is referred to as a "homogeneous catalyst".^[25] Therefore, development of methods that lead to the preparation of heterogeneous catalysts in a simple and green environment remains an active area of research.

Heterogeneous catalysts are cheaper and have always been one of the most important goals for chemists in industrial development. Recently, various clay materials as efficient catalytic substrate have been utilized for organic synthesis because of their unique features such as numerous abundance, low cost, and good physicochemical properties.^[26-28] Of interest is SEP being a hydrated magnesium silicate clay mineral with a large specific surface area, appropriate mechanical resistance, and fibrous morphology.^[29] Despite these advantages, its difficult separation from the reaction mixture limits the application of SEP as a catalyst substrate in organic transformations.^[30] The modification of SEP fibers with the iron oxide component seems to be a proper way to overcome this limitation. The magnetic property enables easy catalyst recovery from the organic reactions by applying an external magnetic field. Therefore, we designed an efficient, stable, inexpensive, and heterogeneous copper catalyst that performs carbon-sulfur bond formation reactions for the synthesis of *S*-aryl carbamodithioate compounds.

2 | RESULTS AND DISCUSSION

The SEP/Fe₃O₄/CuO catalyst employed for C—S coupling was synthesized according to the literature procedure. We developed a recyclable inexpensive catalyst for the synthesis of *S*-aryl dithiocarbamates. The resulted nanocatalyst was characterized using various characterization techniques such as FT-IR, XRD, FE-SEM, EDX, VSM, and ICP.

The FT-IR spectrum of SEP (a), SEP/Fe₃O₄ (b), and SEP/Fe₃O₄/CuO (c) is depicted in Figure 1. In spectrum (a), the stretching vibration at 1,657 cm^{-1} can be attributed to the water of zeolite, $1,215 \text{ cm}^{-1}$ to the Si-O bands vibration, and the bands at 1.013 and 470 cm^{-1} can be assigned as Si-O-Si vibration.^[31] The absorption bands at 3,686 and 3,555 cm⁻¹ correspond to the OH groups of Mg-OH. Figure 1 (b) shows the FT-IR spectrum of SEP/Fe₃O₄. The typical bands that appear at $437-647 \text{ cm}^{-1}$ are caused by the Fe–O stretching vibration, and the band located at around $1,012 \text{ cm}^{-1}$ is due to the Si-O-Fe linkage. The absorption band at $3,554 \text{ cm}^{-1}$ shows the stretching vibrations of the hydroxyl groups in Fe₃O₄ and water.^[32] The FT-IR spectrum of the final catalyst (SEP/Fe₃O₄/CuO) is indicated in Figure 1c. In comparison, the SEP/Fe₃O₄/CuO has a new absorption band than SEP/Fe₃O₄. The band observed at $1,369 \text{ cm}^{-1}$ is assigned to the bending vibration of Cu–O bond.

Figure 2 shows the XRD profiles of the SEP, SEP/-Fe₃O₄, and SEP/Fe₃O₄/CuO nanocomposites. For the SEP sample, the diffraction peaks at $2\theta = 19.9^{\circ}$, 20.8°, 23.9°, 26.9°, 28.2°, 35.1°, 36.9°, 39.8°, 43.7°, and 59.6° correspond to the (060), (131), (260), (080), (331), (371), (202), (541), (412), and (791) planes (JCPDS No. 13-0595), respectively.^[33] The XRD pattern of the SEP/Fe₃O₄ depicts some new peaks at 2 θ values of 30.3°, 35.7°, 43.4°, 57.5°, and 63.1°, which can be assigned to (220), (311), (400), (511), and (440) crystalline planes of magnetite (JCPDS No. 19-0629), respectively.^[34] In the case of the SEP/Fe₃O₄/CuO sample, a new diffraction peak at 39.1° (200) can be ascribed to the monoclinic CuO according to JCPDS No. 02-1041.^[35] The peaks at $2\theta = 35.8^{\circ}$ (002),







FIGURE 1 The FT-IR spectrum of sepiolite (a), SEP/Fe₃O₄ (b), and SEP/Fe₃O₄/CuO (c)



FIGURE 2 XRD patterns of SEP, SEP/Fe₃O₄, and SEP/Fe₃O₄/ CuO nanocomposites

53.9° (202), and 58.3° (202) are also overlapped with the diffraction peaks of SEP and Fe_3O_4 in the prepared nanocomposite, which makes it difficult to identify the crystal structure of CuO particles. In addition, the reduction in peak intensities is caused by the surface coverage of the SEP/Fe₃O₄ sample by CuO particles.

The surface morphologies of different samples are illustrated in Figure 3. As can be seen, the SEP presents a needle-like morphology. In SEP/Fe₃O₄/CuO, larger quantities of nanoparticles in spherical shape are dispersed on the SEP support.

The catalyst surface presents some characteristic peaks in the EDX spectrum (Figure 4), which confirms the presence of Fe and Cu, along with other species, including O, Mg, and Si elements. From the EDX spectrum of SEP/Fe₃O₄/CuO composite, the existence of Fe and Cu element energy peaks confirms the successful deposition of iron oxide and cupric oxide crystals on the surface of SEP fibers.

In addition, the element distribution of SEP/Fe₃O₄/ CuO (Figure 5) indicates the uniform deposition of the Fe₃O₄ and CuO nanoparticles on the SEP support.

The magnetic behavior of the as-prepared SEP/-Fe₃O₄/CuO was studied to evaluate the possibility of magnetic separation and recycling of this catalyst. The magnetic hysteresis curves of the SEP/Fe₃O₄ and SEP/-Fe₃O₄/CuO nanocomposites are displayed in Figure 6. As shown, the magnetization saturation (M_s) values decrease from 30.4 emu g⁻¹ (SEP/Fe₃O₄) to 9.0 emu g⁻¹ (SEP/Fe₃O₄/CuO), which could be attributed to the existence of nonmagnetic CuO material. However, the level of magnetism of the SEP/Fe₃O₄/CuO catalyst is enough to separate the catalyst using an external magnetic field.

On the basis of ICP-OES analysis, the weight percentage of Cu was obtained equal to 16.19%.

After characterization, the catalyst activity was checked in the C—S cross-coupling reaction for the synthesis of the *S*-aryl dithiocarbamates (Scheme 1). First, the reactions of the secondary amine, aryl iodide, and carbon disulfide under various conditions were investigated to set up the optimal conditions. The results are summarized in Table 1.

To optimize the reaction conditions, the mixture of morpholine (1.2 mmol), 4-iodo anisole (1.0 mmol), CS_2 (2.0 mmol), K_2CO_3 (1.2 mmol), and 20 mg catalyst in 2 ml of DMF under air atmosphere at 80°C was selected as a model reaction. This reaction was also carried out at several temperatures, for which the highest efficiency was obtained at 100°C (Table 1, entries 2–3).

When the reaction solvent was reduced to 1 ml, the reaction efficiency increased significantly (Table 1, entry 4). The time to complete the reaction was checked by TLC, as shown in Table 1 (entries 4, 5, 20, 21). The reaction efficiency did not differ from 12 to 24 hr, so 12 hr was selected as the best time. No products were obtained when the mentioned reaction was performed in DMSO, Dioxane, and EtOH as solvent (Table 1, entries 12-14). The reaction efficiency also decreased when using water and DMF as solvents (Table 1, entry 18). By increasing the catalyst amount to 40 mg, there was a significant decrease in efficiency, so 20 mg of catalyst was selected (Table 1, entries 6-7). In addition, some other different bases such as Et₃N, Na₂CO₃, and K₃PO₄ were examined. Best yields were obtained when applying K_2CO_3 or Et_3N were used as bases (Table 1, entries 5 and 15). This reaction was also carried out with different amounts of morpholine and carbon disulfide. As can be seen in Table 1, the optimized amount of morpholine was 1.2 mmol and CS₂ 2 mmol. Performing



FIGURE 3 FE-SEM images of SEP/Fe₃O₄/CuO nanocomposite



FIGURE 4 EDX spectrum of SEP/Fe₃O₄/CuO nanocomposite

this reaction under N_2 atmosphere showed no difference compared with that under air atmosphere (Table 1, entries 5 and 19). No product was formed when performing the reaction in the absence of a catalyst and during the use of sepiolite (C₁) and SEP/Fe₃O₄ (C₂) as catalysts (Table 1, entry 22–24). With the optimal conditions determined, a variety of aryl halides and secondary amines were subjected to optimal conditions, and the results are shown in Table 2. Most products were known and characterized by melting point (mp), IR, ¹H NMR, and ¹³C NMR data as well as by comparing their physical data with those in the literature. Also, new products synthesized by elemental analysis (CHNS) were approved.

The IR spectrum of compound **3a** exhibited absorption bands in the area of 2,854 and 2,924 cm⁻¹ for the CH₂ groups of morpholine ring. The ¹H NMR spectrum showed protons of the aromatic ring in the field of 7.01–7.37 ppm. Protons of morpholine (CH₂) appeared at 3.71–3.74 and 4.07–4.20 ppm. The OCH₃ proton was seen as a singlet at $\delta = 3.83$ ppm. The ¹³C NMR spectrum of 3a exhibited eight signals that are consistent with the proposed structure. The presence of a peak in the area of 197.1 ppm indicates the presence of a C=S bond.

The recyclability of the catalyst was checked during the preparation of product **2a**. After the reaction was completed in the first run, an external magnet was used nanocomposite

stand for Mg) for SEP/Fe₃O₄/CuO





FIGURE 6 VSM of SEP/Fe₃O₄/CuO nanocomposite

for the separation of the catalyst from the reaction mixture. The recycled catalyst was washed twice with ethyl acetate, dried at ambient temperature, and used for the next run. The reaction was repeated for up to three consecutive runs, and the results of which are shown in Figure 7.

Moreover, the XRD pattern (Figure 8) of the SEP/-Fe₃O₄/CuO catalyst after catalytic test did not show any significant variation in the crystal structure, implying the excellent stability of the SEP/Fe₃O₄/CuO nanocomposite. The FT-IR spectrum (Figure 9) of the nanocomposite after three uses showed no changes. Also on the basis of ICP-OES analysis, the percentage of copper weight decreased from 16.19% to 15.83%.

Scheme 2 shows the proposed mechanism for the coupling reaction of three components between secondary amines, carbon disulfide, and aryl iodides. According to the previously reported mechanisms, first, the reaction of a carbondisulfide with secondary amine gives the dithiocarbamate anion, and then the oxidation of catalyst is taken place by an aryl iodide. Finally, the crosscoupling reaction of aryl iodide and dithiocarbamate anion followed by a reductive elimination yields the corresponding S-aryl-carbamodithioate as the main products, and this expands the catalytic cycle.

To show the efficacy of the SEP/Fe3O4/CuO nanoparticles for the synthesis of S-aryl dithiocarbamates, the results of this method were compared with some previously reported catalysts for compounds 1a and 4a (Table 3).

3 **EXPERIMENTAL**

3.1 Materials and methods

The natural sepiolite used for the preparation of catalyst was purchased from Dorkav Minig Company (Mashhad, Iran). Before using in the experiments, the SEP sample was purified according to the literature.^[37] For SEP/-Fe₃O₄/CuO preparation, analytical-grade of ferric chloride hexahydrate (FeCl₃·6H₂O), ferrous sulfate heptahydrate (FeSO₄·7H₂O), ammonia solution (25%), copper acetate monohydrate (Cu[OAc]₂·H₂O), and sodium hydroxide (NaOH) were purchased from Merck (Darmstadt, Germany). All solvents and materials purchased from Merck chemical company and solvents for the reaction were distilled before use: DMF, 1, 4-dioxane, DMSO, ethanol, n-hexane, and ethyl acetate. All the

TABLE 1 Optimization of reaction conditions for S-aryl dithiocarbamates

H ₃ CO	+ N H	+ cs ₂ -	Cataly Base, Salvent, ⁻	/st Temperature	H ₃ CO	S S 3a	0		
Entry	Catalyst amount (mg)	Morpholin	CS ₂ (Mol ratio)	Base	Solvent	Т (°С)	Time (h)	Atmosphere	Yield ^a (%)
1	$C_3^{b}(20)$	1.2	2	K ₂ CO ₃	DMF (2 cc)	80	24	Air	31
2	C ₃ (20)	1.2	2	K_2CO_3	DMF (2 cc)	100	24	Air	45
3	C ₃ (20)	1.2	2	K_2CO_3	DMF (2 cc)	120	24	Air	23
4	C ₃ (20)	1.2	2	K_2CO_3	DMF (1 cc)	100	24	Air	54
5	C ₃ (20)	1.2	2	K ₂ CO ₃	DMF (1 cc)	100	12	Air	54 ^c
6	C ₃ (40)	1.2	2	K ₂ CO ₃	DMF (1 cc)	100	12	Air	45
7	C ₃ (10)	1.2	2	K_2CO_3	DMF (1 cc)	100	12	Air	38
8	C ₃ (20)	1.2	3	K_2CO_3	DMF (1 cc)	100	12	Air	15
9	C ₃ (20)	1.2	1.5	K_2CO_3	DMF (1 cc)	100	12	Air	8
10	C ₃ (20)	2	2	K_2CO_3	DMF (1 cc)	100	12	Air	15
11	C ₃ (20)	1.5	2	K_2CO_3	DMF (1 cc)	100	12	Air	54
12	C ₃ (20)	1.2	2	K_2CO_3	Dioxane (1 cc)	100	12	Air	0
13	C ₃ (20)	1.2	2	K_2CO_3	DMSO (1 cc)	100	12	Air	0
14	C ₃ (20)	1.2	2	K_2CO_3	EtOH (1 cc)	100	12	Air	0
15	C ₃ (20)	1.2	2	Et ₃ N	DMF (1 cc)	100	12	Air	54
16	C ₃ (20)	1.2	2	Na ₂ CO ₃	DMF (1 cc)	100	12	Air	31
17	C ₃ (20)	1.2	2	K_3PO_4	DMF (1 cc)	100	12	Air	38
18	C ₃ (20)	1.2	2	K ₂ CO ₃	$\begin{array}{l} \text{DMF: 0.8 cc} \\ + \text{H}_2\text{O:0.2 cc} \end{array}$	100	12	Air	46
19	C ₃ (20)	1.2	2	K_2CO_3	DMF (1 cc)	100	12	N_2	54
20	C ₃ (20)	1.2	2	K ₂ CO ₃	DMF (1 cc)	100	6	Air	23
21	C ₃ (20)	1.2	2	K_2CO_3	DMF (1 cc)	100	9	Air	38
22	$C_1^{d}(20)$	1.2	2	K ₂ CO ₃	DMF (1 cc)	100	12	Air	0
23	$C_2^{e}(20)$	1.2	2	K_2CO_3	DMF (1 cc)	100	12	Air	0
24	0	1.2	2	K ₂ CO ₃	DMF (1 cc)	100	12	Air	0

Note: Reaction conditions: mopholine (1.2 mmol), 4-Iodo anisole (1 mmol), catalyst, CS₂ (2 mmol), base (1.2 mmol) in 1.0 ml of solvent for 12 hr. The blod values are for highlighting optimized conditions.

^aIsolated yield.

^bC₃: SEP/Fe₃O₄/CuO.

^cOptimized conditions.

 ${}^{d}C_{1}$: sepiolite.

^eC₂: SEP/Fe₃O₄.

reactions were performed in sealed tubes and monitored by TLC. The products were purified by thin-layer chromatography (TLC) plates (silica gel G). IR spectra were recorded on a BRUKER Tensor-27 FT-IR spectrophotometer using KBr pellets, and all melting points were measured on an Electrothermal-9,100 apparatus. Proton nuclear magnetic resonance spectra (¹H NMR) and carbon nuclear magnetic resonance spectra (¹³C NMR) were recorded on a Bruker 300 AVANCE III NMR magnet (300 MHz for ¹H NMR and 75 MHz for ¹³C NMR) using DMSO-d₆ as a solvent. Field emission scanning electron microscopy (FE-SEM) studies were performed on a SIGMA VP microscope (Zeiss, Germany) equipped with an energy-dispersive X-ray (EDX) system. The X-ray diffraction (XRD) analysis was carried out using an X'Pert PRO powder diffractometer (PANalytical B.V.,

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TABLE 2 Synthesis of S-aryl dithiocarbamates

Entry	Compounds	Secondary amine	Aryl iodide	Product	Yield (%)
1	la	HN O		S S S	76
2	2a	HN O		S S S	67
3	3a	HN J	H ₃ CO	H ₃ CO S N	54
4	4a	HN O	CI	CI S S	77
5	5a	HN		S N	60
6	6a	HN		S N	80
7	7a	HN	H ₃ CO	H ₃ CO S N	68
8	8a	HN	CI	CI S S	65
9	9a	HN_		S N S	82
10	10a	HN		S N	76
11	11a	HN	H ₃ CO	H ₃ CO S N	64

(Continues)

Yield (%)

70

TABLE 2 (Continued)



FIGURE 7 Reusability of SEP/Fe₃O₄/CuO in the compound 2a



FIGURE 8 XRD patterns of SEP/Fe₃O₄/CuO nanocomposite before and after catalytic reaction

Netherlands) using Cu K α radiation ($\lambda = 0.154$ nm). The magnetic property of the samples was determined using a vibrating-sample magnetometer (VSM) (Meghnatis Daghigh Kavir Co., Iran) at room temperature. The residual copper concentration was quantified by an inductively coupled plasma-optical emission spectrometer (ICP-OES, 7900, AGILENT, USA).

3.2 | Catalyst preparation

The SEP/Fe₃O₄ nanocomposite was prepared by coprecipitation of $FeSO_4 \cdot 7H_2O$ and $FeCl_3 \cdot 6H_2O$, in the

Wavenumber cm-1 **FIGURE 9** FT-IR of SEP/Fe₃O₄/CuO nanocomposite: a) before; and b) after catalytic reaction

2000

1500

1000

500

2500

3500

3000

presence of the purified SEP. First, 4.0 g of SEP powder was added to a beaker (300 ml) that contained 200 ml of FeCl₃·6H₂O (0.06 M) and FeSO₄·7H₂O (0.03 M) solution. The mixture was sonicated for 15 min under nitrogen atmosphere at 40°C. Then, 11 ml of aqueous ammonia (25% w/w) was added dropwise into the mixture with vigorous stirring at 60°C. Nitrogen stream was employed during the reaction to prevent critical oxidation. After aging for 2 hr at 60°C, the prepared SEP/Fe₃O₄ nanocomposite was collected with a magnet and washed with pure water several times. The product was dried at 60° C in a vacuum drying oven overnight.

The SEP/Fe₃O₄/CuO nanocomposite was prepared with a facile solvothermal procedure. Briefly, 3.0 g of the SEP/Fe₃O₄ nanocomposite was dispersed into 110 ml ethanolic solution of Cu(OAc)₂·H₂O (0.15 M) for 30 min. In the next step, 1.0 g of NaOH pellets was added to the mixture. After mixing for 5 min, the resulting mixed solution was poured into a Teflon-lined stainless steel autoclave (150 ml), sealed, and then heated at 130°C for 24 hr. Finally, the black product was rinsed with absolute ethanol and distilled water for several times, and then dried at 60°C overnight (Scheme 3). **SCHEME 2** Proposed mechanism for the synthesis of *S*-aryl dithiocarbamates



 $-CuO \equiv SEP/Fe_3O_4/CuO$

TABLE 3 Comparison of the reaction between secondary amines, carbon disulfide, and aryl iodides (compounds **1a** and **4a**) in the presence of SEP/Fe₃O₄/CuO nanocomposite and some previously reported catalysts

Entry	Product	Catalyst	Time (hr)	Yield (%)	Ref.
1	1a	Cu(II) nanocatalyst supported on modified AlPO ₄	17	82	36
2	1a	Fe ₃ O ₄ -CuO MNPs	10	80	20
3 ^a	1a	SEP/Fe ₃ O ₄ /CuO	12	76	-
4	4a	Fe ₃ O ₄ -CuO MNPs	12	65	20
5 ^a	4a	SEP/Fe ₃ O ₄ /CuO	12	77	

^aPresent work.

3.3 | General procedure for the synthesis of *S*-aryl dithiocarbamates (1–12a)

In a sealed tube with a magnetic stir-bar in room temperature, CS_2 (2 mmol), aryl iodide (1.0 mmol), K_2CO_3 (1.2 mmol), and SEP-Fe₃O₄-CuO (20 mg) were added to secondary amine (1.2 mmol) in 1 ml of DMF. After 30 min, the reaction mixture was heated at 100°C for 12 hr (checked by TLC). After accomplishment of the reaction, the reaction mixture was extracted with ethyl acetate and purified by thin-layer chromatography (TLC) plates (silica gel) using n-hexane/ethyl acetate (4:2) affording the desired products.

3.4 | Phenyl morpholine-4-carbodithioate (1a)^[38]

Light brown solid, mp 137–139°C. IR (KBr): 1,188, 1,575, 2,849, 2,920 cm⁻¹.

¹H NMR (300 MHz, DMSO-d₆) δ (ppm): 3.72–3.75 (m, 4H, 2CH₂), 4.08–4.21 (broad, 4H, 2CH₂),

7.44–7.53 (m, 5H, arom). 13 C NMR (75 MHz, DMSO-d_6) δ (ppm): 51.7, 66.1, 129.6, 130.5, 131.1, 137.3, 195.9.

3.5 | *P*-Tolyl morpholine-4-carbodithioate (2a)^[39]

Yellow solid, mp 134–137°C. IR (KBr): 1,175, 1,589, 2,852, 2,916, 2,972 cm⁻¹.

¹H NMR (300 MHz, DMSO-d₆) δ (ppm): 2.38 (s, 3H, CH₃), 3.71–3.74 (m, 4H, 2CH₂), 4.07–4.20 (broad, 4H, 2CH₂), 7.29 (d, J = 8.3 Hz, 2H, arom), 7.33 (d, J = 8.5 Hz, 2H, arom). ¹³C NMR (75 MHz, DMSO-d₆) δ (ppm): 21.4, 51.7, 66.1, 127.7, 130.3, 137.2, 140.4, 196.4.

3.6 | 4-Methoxyphenyl morpholine-4-carbodithioate (3a)^[39]

Yellow solid, mp 133–135°C. IR (KBr): 1,166, 1,588, 2,854, 2,924, 2,957 cm⁻¹.



SCHEME 3 Synthesis of SEP-Fe₃O₄-CuO

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¹H NMR (300 MHz, DMSO-d₆) δ (ppm): 3.73 (t, J = 4.9 Hz, 4H, 2CH₂), 3.83 (s, 3H, OCH₃), 4.07–4.20 (broad, 4H, 2CH₂), 7.03 (d, J = 8.8 Hz, 2H, arom), 7.35 (d, J = 8.8 Hz, 2H, arom). ¹³C NMR (75 MHz, DMSO-d₆) δ (ppm): 51.2, 55.8, 66.1, 115.2, 121.7, 139.0, 161.2, 197.1.

3.7 | 4-Chlorophenyl morpholine-4-carbodithioate (4a)^[20]

Yellow solid, mp 111–113°C. IR (KBr): 1,176, 1,570, 2,853, 2,920 cm⁻¹.

¹H NMR (300 MHz, DMSO-d₆) δ (ppm): 3.73 (t, J = 4.9 Hz, 4H, 2CH₂), 4.06–4.20 (broad, 4H, 2CH₂), 7.46 (d, J = 8.4 Hz, 2H, arom), 7.55 (d, J = 8.6 Hz, 2H, arom). ¹³C NMR (75 MHz, DMSO-d₆) δ (ppm): 51.9, 66.1, 129.7, 130.1, 135.8, 139.1, 195.2.

3.8 | Phenyl piperidine-1-carbodithioate (5a)^[38]

Yellow solid, mp 110–112°C. IR (KBr): 1,226, 1,576, 2,852, 2,926, 2,988 cm⁻¹.

¹H NMR (300 MHz, DMSO-d₆) δ (ppm): 1.63–1.68 (m, 6H, 3CH₂), 4.02–4.22 (m, 4H, 2CH₂), 7.42–7.51 (m, 5H,

arom). ¹³C NMR (75 MHz, DMSO-d₆) δ (ppm): 24.0, 25.7, 26.4, 52.1, 53.1, 129.5, 130.3, 131.6, 137.4, 194.0.

3.9 | *p*-Tolyl piperidine-1-carbodithioate (6a)^[39]

Yellow solid, mp 115–118°C. IR (KBr): 1,171, 1,592, 2,852, 2,935, 2,994 cm⁻¹.

¹H NMR (300 MHz, DMSO-d₆) δ (ppm): 1.62–1.70 (m, 6H, 3CH₂), 2.37 (s, 3H, CH₃), 4.00–4.21 (m, 4H, 2CH₂), 7.27 (d, J = 8.3 Hz, 2H, arom), 7.31 (d, J = 8.3 Hz, 2H, arom). ¹³C NMR (75 MHz, DMSO-d₆) δ (ppm): 21.4, 24.0, 25.7, 26.4, 52.0, 53.1, 128.2, 130.2, 137.3, 140.2, 194.5.

3.10 | 4-Methoxyphenyl piperidine-1-carbodithioate (7a)^[39]

White solid, mp 93–96°C. IR (KBr): 1,246, 1,590, 2,852, 2,921, 2,997 cm⁻¹.

¹H NMR (300 MHz, DMSO-d₆) δ (ppm): 1.62–1.68 (m, 6H, 3CH₂), 3.83 (s, 3H, OCH₃), 4.00–4.21 (m, 4H, 2CH₂), 7.02 (d, J = 8.5 Hz, 2H, arom), 7.34 (d, J = 8.3 Hz, 2H, arom). ¹³C NMR (75 MHz, DMSO-d₆) δ (ppm): 24.0, 25.7, 26.4, 51.9, 53.2, 55.8, 115.1, 115.5, 122.3, 132.5, 139.0, 161.1, 195.3.

3.11 | 4-Chlorophenyl piperidine-

1-carbodithioate (8a)^[20]

Yellow solid, mp 85–88°C. IR (KBr): 1,223, 1,569, 2,851, 2,936 cm⁻¹.

¹H NMR (300 MHz, DMSO-d₆) δ (ppm): 1.64–1.67 (m, 6H, 3CH₂), 3.99–4.20 (m, 4H, 2CH₂), 7.43 (d, J = 8.5 Hz, 2H, arom), 7.52 (d, J = 8.5 Hz, 2H, arom). ¹³C NMR (75 MHz, DMSO-d₆) δ (ppm): 24.0, 25.6, 26.5, 52.2, 53.2, 129.5, 130.6, 135.6, 139.1, 193.3.

3.12 | Phenyl pyrrolidine-1-carbodithioate (9a)^[38]

Yellow solid, mp 92–94°C. IR (KBr): 1,158, 1,577, 2,870, 2,960 cm⁻¹.

¹H NMR (300 MHz, DMSO-d₆) δ (ppm): 1.89–2.13 (m, 4H, 2CH₂), 3.77 (t, J = 6.9 Hz, 4H, 2CH₂), 7.45–7.51 (m, 5H, arom). ¹³C NMR (75 MHz, DMSO-d₆) δ (ppm): 24.3, 26.3, 51.5, 55.7, 129.5, 130.4, 131.2, 137.1, 191.0.

3.13 | *P*-Tolyl pyrrolidine-1-carbodithioate (10a)

Yellow solid, mp 118–120°C. IR (KBr): 1,177, 1,592, 2,866, 2,963 cm⁻¹.

¹H NMR (300 MHz, DMSO-d₆) δ (ppm): 1.89–2.13 (m, 4H, 2CH₂), 2.37 (s, 3H, CH₃), 3.77 (t, J = 7.1 Hz, 4H, 2CH₂), 7.28 (d, J = 8.2 Hz, 2H, arom), 7.32 (d, J = 8.3 Hz, 2H, arom). ¹³C NMR (75 MHz, DMSO-d₆) δ (ppm): 21.4, 24.3, 26.3, 51.4, 55.7, 127.8, 130.2, 137.0, 140.2, 191.5.

Anal. Calcd. For $C_{12}H_{15}NS_2$: C, 60.72; H, 6.37; N, 5.90; S, 27.01%. Found. C, 60.35; H, 6.42; N, 5.95; S, 27.21%.

3.14 | 4-Methoxyphenyl pyrrolidine-1-carbodithioate (11a)^[40]

Yellow solid, mp 102–104°C. IR (KBr): 1,161, 1,590, 2,871, 2,956, 3,010 cm⁻¹.

¹H NMR (300 MHz, DMSO-d₆) δ (ppm): 1.91–2.10 (m, 4H, 2CH₂), 3.74–3.78 (m, 4H, 2CH₂), 3.82 (s, 3H, OCH₃), 7.03 (d, J = 8.3 Hz, 2H, arom), 7.34 (d, J = 8.2 Hz, 2H, arom). ¹³C NMR (75 MHz, DMSO-d₆) δ (ppm): 24.3, 26.4, 51.3, 55.7, 55.8, 115.1, 121.9, 138.7, 161.1, 192.1.

3.15 | 4-Chlorophenyl pyrrolidine-1-carbodithioate (12a)

Yellow solid, mp 105–108°C. IR (KBr): 1,178, 1,593, 2,867, 2,963 cm⁻¹.

¹H NMR (300 MHz, DMSO-d₆) δ (ppm): 1.89–2.12 (m, 4H, 2CH₂), 3.73–3.79 (m, 4H, 2CH₂), 7.45 (d, J = 8.5 Hz, 2H, arom), 7.54 (d, J = 8.6 Hz, 2H, arom). ¹³C NMR (75 MHz, DMSO-d₆) δ (ppm): 24.4, 26.4, 51.5, 55.8, 129.6, 130.2, 135.6, 138.8, 190.3.

Anal. Calcd. For $C_{11}H_{12}CINS_2$: C, 51.25; H, 4.69; N, 5.43; S, 24.87%. Found. C,51.53; H, 4.60; N, 5.50; S, 24.90%.

4 | CONCLUSIONS

In summary, SEP clay was utilized to synthesize the magnetically recyclable and highly efficient SEP/Fe3O4/CuO nanocomposite. The catalytic activity of the prepared nanocomposite was tested in the reaction of phenyl iodide, secondary amines, and CS2 for the synthesis of Saryl dithiocarbamates. Various S-aryl dithiocarbamates were synthesized under benign reaction conditions while offering satisfactory yield. The ICP analysis results showed a negligible Cu leaching for the catalyst during the reaction process, proving that the heterogeneous catalyst is stable and very active under the applied conditions. As a result, the advantages offered by this procedure are as follows: operational simplicity, use of cheap copper catalyst, good product efficiency, short reaction time, and providing recyclability of catalyst up to three times without considerable loss in efficiency. Additionally, the catalyst could be easily separated from the reaction mixture by using an external magnet.

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