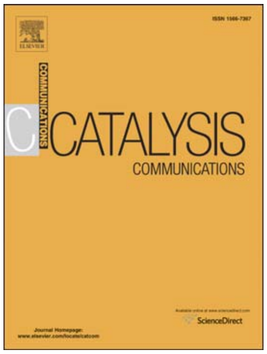

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The use of *κ*-Carrageenan/Fe_3O_4 nanocomposite as a nanomagnetic catalyst for clean synthesis of rhodanines

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Abstract: In this work, magnetically separable Fe_3O_4 nanoparticles were synthesized in the presence of natural κ-carrageenan (KCAR) biopolymer to provide Fe_3O_4@KCAR. FT-IR analysis, scanning electron microscope (SEM), X-ray diffraction, VSM analysis, and SEM-EDAX were incorporated for the characterization of Fe_3O_4@KCAR nanocomposite. And then, the first catalytic report of Fe_3O_4@KCAR with no post-modification was achieved by studying its catalytic activity in the multicomponent reaction of rhodanine synthesis. Based on this study, Fe_3O_4@KCAR was an efficient, magnetically separable and recyclable, water-dispersible and green catalyst with natural source. This catalyst also showed 9 run recyclability with no significant yield decrease.

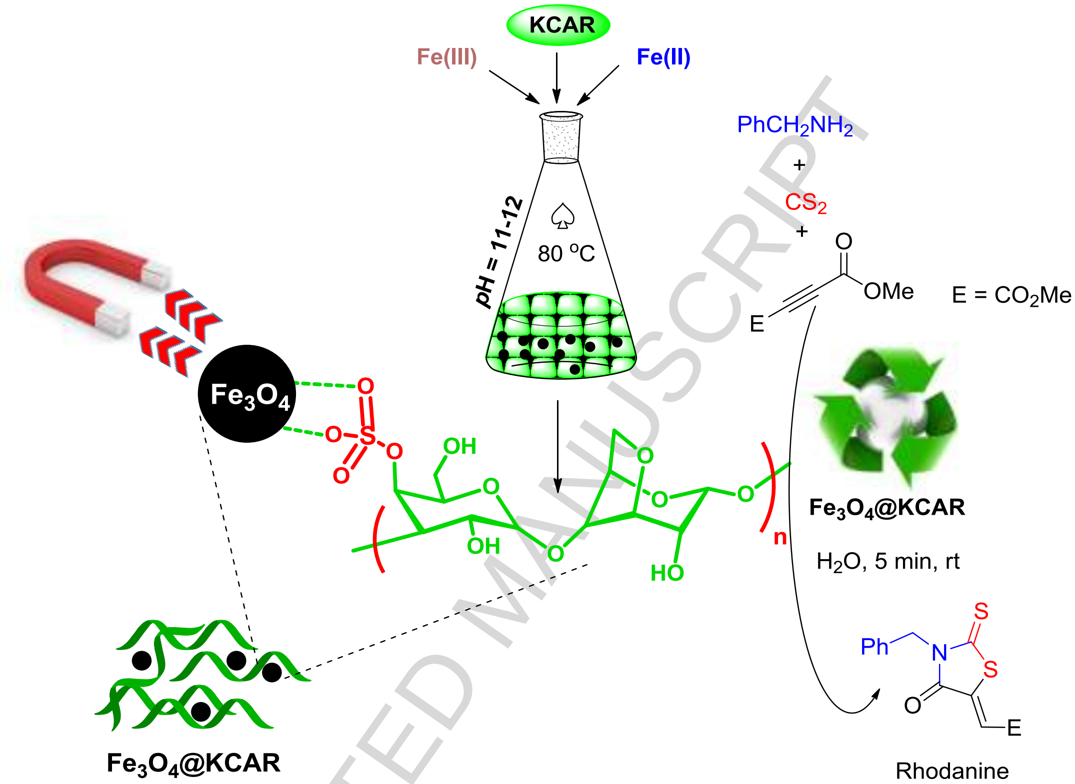
Keywords: Magnetic nanocomposite; Fe_3O_4; κ-carrageenan (KCAR); Fe_3O_4@KCAR; rhodanine.

Introduction

Magnetically recoverable nanocatalysts give raise in the sustaining and greening the chemical processes [1-4]. These are very suitable alternative to replace with equimolar, toxic and harsh reagents, owing to their simple work-up and separation and ability to reuse in next runs [5]. Beyond it, they can be doped, modified, coated, encapsuled, and functionalized with various organic, inorganic and even hybrid precursors such as polymers, silica sources, and organosiloxanes, respectively. Among them, polymers have taken an advantages especially biodegradable and natural polymers with active catalytic centers are interesting for research. In this case, the toxicity, steps of catalyst preparation decrease. On the other hand, by modification of polymer surface, a catalyst with tunable activity and favorable functionalities can be obtained.

Polymers such as poly(styrene-methacrylic acid) [6], chitosan [7-9], poly(ethyleneglycol) (PEG) [10], polyethyleneimine (PEI) [11, 12], polyvinylidene fluoride (PVDF) [13] are currently used for magnetization with Fe_3O_4 nanoparticles. Also, some copolymers and nanocomposites are designed to produce and magnetic nanocomposites [14-18]. κ-Carrageenan (KCAR) is of those polymers which has been used to fabricate various nanocomposites [19, 20]. However, Pericàs *et al.* [21] functionalized carrageenan and further modified it to obtain a heterogeneous and magnetic organocatalyst. In spite of these investigations, there is no catalytic study on the κ-Carrageenan/Fe_3O_4 nanocomposites (Fe_3O_4@KCAR) which could be used with no further modification or extra polymers. Hence we aimed to synthesize and discuss about the catalytic activity of Fe_3O_4@KCAR which is directly incorporated as a catalyst in three-component synthesis of rhodanine derivatives through condensation of an amine, CS_2, and dialkyl acetylenedicarboxylate (DRAD) under aqueous conditions at room temperature. This was to obtain the catalytic behavior of Fe_3O_4@KCAR under neutral conditions. Due to the natural source of KCAR and hence, its biodegradability, active functions (-SO_3^- and -OH groups), and ability to bind to the surface of Fe_3O_4 through -SO_3^- and -OH groups, we wished to examine its catalytic activity in the organic reactions. In this paper, we have synthesized Fe_3O_4 in the presence of KCAR under alkali conditions to obtain Fe_3O_4@KCAR nanocomposite. This small amount was enough to catalyze the synthesis of rhodanine.

Synthesis of bioactive rhodanine based heterocycles is a key step in the producing biologically interesting heterocycles [22-24]. On the other hand, their green and non-toxic synthesis can accelerate and facilitate the separation, purification steps. Therefore, the obtained product by green approach may be trustful for biological uses and investigations. Our proposed nanomagnetic catalyst can play an important part in the synthesis of such compounds. A schematic pathway for synthesis of Fe_3O_4@KCAR and rhodanine are shown in Scheme 1.



Scheme 1. A schematic pathway for synthesis of Fe_3O_4@KCAR and rhodanine.

2. Experimental

2.1. Catalytic preparation (Fe_3O_4-KCAR)

In a typical synthesis, 2 g of KCAR (obtained from Condinson Co. Denmark) was dissolved in 100 mL distilled water. Then, $FeCl_3.6H_2O$ (5 g) and $FeCl_2.4H_2O$ (2 g) were slowly added into the mixture. The mixture was stirred strongly at 80 ^{o}C to obtain a clear solution, and then aqueous ammonia was added to solution until the *p*H of 12. Then the solution was kept at 80 ^{o}C under vigorous stirring for further 30 min. The precipitate was collected with an external magnet and washed with water and methanol for several times dried in vacuum for 6 h. After that, the final product was washed with water in the presence of an external magnet.

2.2. Catalytic test

In a typical method, 1 mmol of benzylamine, 1 mmol of dimethyl acetylenedicarboxylate (DMAD) were mixed together in the presence of water dispersed Fe_3O_4@KCAR (0.01 g/2 mL) and then, water dissolved CS_2 (1 mmol/1 mL) was added to the reaction mixture during 5 min. After 5 min, the color of reaction mixture turned to orange and the reaction completion was monitored by TLC. Finally, an extra amount of water and then dichloromethane were added to solution to stop the reaction and extract the product. Thus, the product was transferred to dichloromethane and the catalyst was separated from mixture with a magnet. Then the dichloromethane was evaporated and the residue was purified by column chromatography if needed. The catalyst was washed with ethanol/ether and used for next cycles (in the case of recyclability test). All the products were previously reported [23, 24] and were characterized by comparing IR and physical data with those (see supporting information). The spectral data for selected product: *Ethyl 2-[3-((4-chlorophenyl)methyl)-4-oxo-2-thioxo-1,3-thiazolan-5-*

yliden]ethanoate [Table 1, Entry 4: see supporting Information]: Orange powder. IR (KBr) (ν_{max}, cm^{-1}): 1728 (CO), 1649 (CC), 1310 and 1177 (CS). ^1H NMR (500 MHz, $CDCl_3$): δ_H = 3.87 (3 H, s, OCH_3), 5.24 (2 H, s, CH_2Ph), 6.84 (1 H, s, C=CH), 7.28 (2 H, d, $^3J_{HH}$ = 8.4 Hz, 2 CH of Ar), 7.37 (2 H, d, $^3J_{HH}$ = 8.4 Hz, 2 CH of Ar) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C = 46.6 (OCH_3), 52.9 (CH_2Ph), 117.2 (C=CH), 128. 9 (2 CH of Ar), 130.5 (2 CH of Ar), 132.8 (C_{ipso} of Cl), 134.4 (C_{ipso} of NC), 141.8 (C=CH), 165.45 (CON), 166.5 (CO_2CH_3), 195.4 (C=S) [25].

3. Results and discussion

In this work, Fe_3O_4 was synthesized in the presence of KCAR which led to the synthesis of Fe_3O_4@KCAR. During the synthesis, KCAR acted as a stabilizer and in after the synthesis, Fe_3O_4 nanoparticles are functionalized by KCAR. Hydroxyl riched KCAR herein can act as a reaction mediator to proceed the reaction. Functionalization of Fe_3O_4 can be performed by both hydroxyl and sulfate groups.

By comparing the FT-IR spectrums of Fe_3O_4@KCAR nanocomposite and KCAR, the presence of KCAR surrounding the Fe_3O_4 can be clearly observed by related peaks can be exclaimed (Figure 1a). The two samples showed the typical absorptions bands of k-carrageenan polysaccharide: ~1230 cm^{-1}, S-O asymmetric sulfate stretch; ~1010-1065 cm^{-1}, C-O and C-OH stretching and 843 cm^{-1}, α(1,3)-D-galactose C-O-S stretch [26] thus indicating that the biopolymer chains maintained their chemical characteristics when in contact with the Fe_3O_4 (see Supporting Information). The EDS of Fe_3O_4@KCAR nanocomposite spectrum indicates that there were only C, O, S and Fe elements in the nanocomposite (Figure 1b). The magnetic hysteresis loops measurements (Figure 1c) of the Fe_3O_4@KCAR indicate that its saturation magnetization value (Ms) is 29.05 emu.g^{-1}.

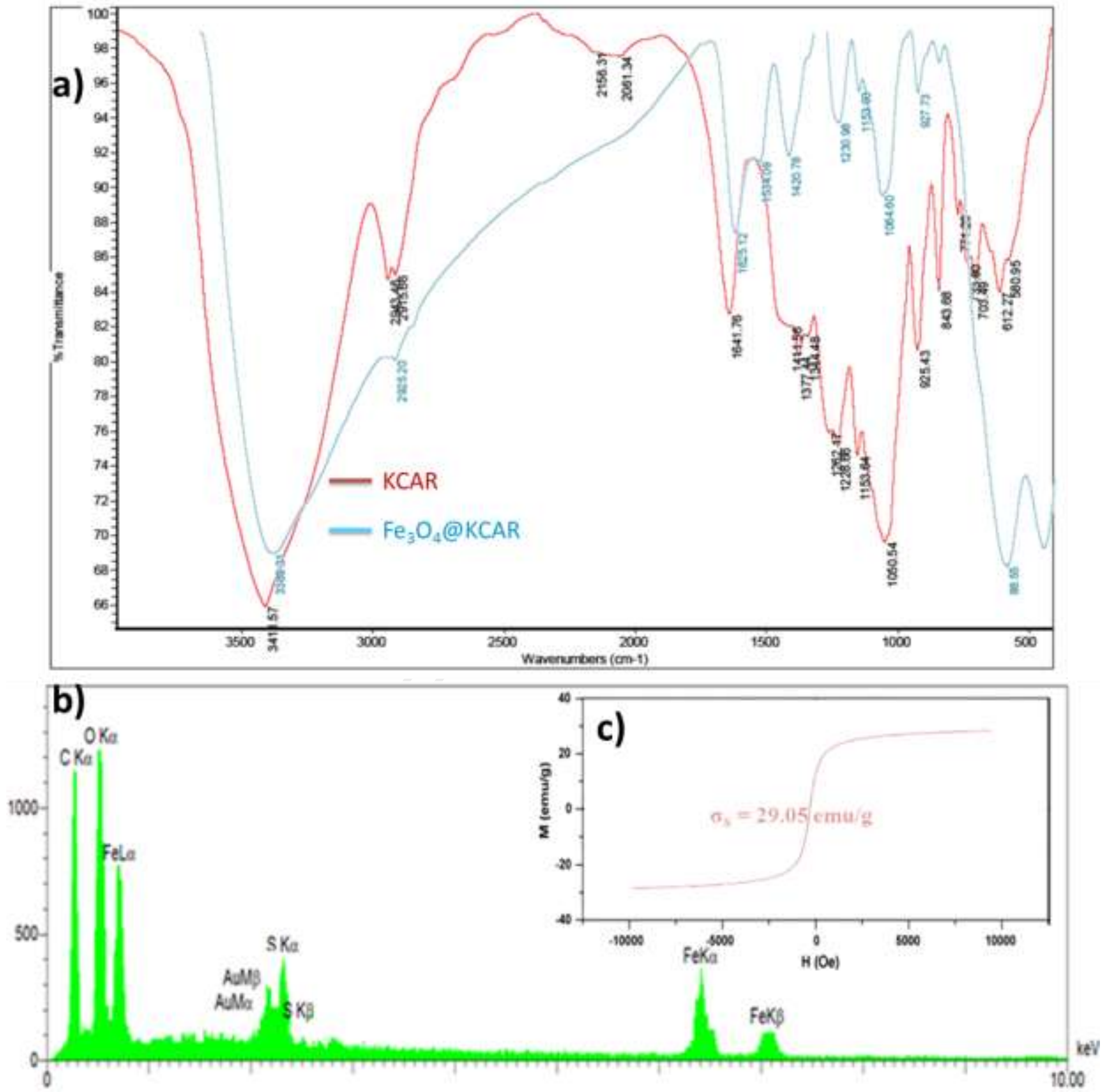


Fig. 1. FT-IR spectrum of KCAR and Fe_3O_4@KCAR (a), EDS (b) and magnetization curves at 300 K (c) of Fe_3O_4@KCAR.

SEM images show the morphology of Fe_3O_4@KCAR. The morphology of the nanocomposite displayed homogeneous structure and the SEM image show a large particles. However, based on the X-ray diffraction, the calculated average crystal size was 19 nm. It shows that Fe_3O_4 nanoparticles are synthesized and embedded inside the KCAR network. Therefore, Fe_3O_4 nanoparticles are surrounded by KCAR and have generated Fe_3O_4@KCAR nanocomposite. Also, X-ray diffraction peaks indicate the presence of formation of Fe_3O_4 (Figure 2).

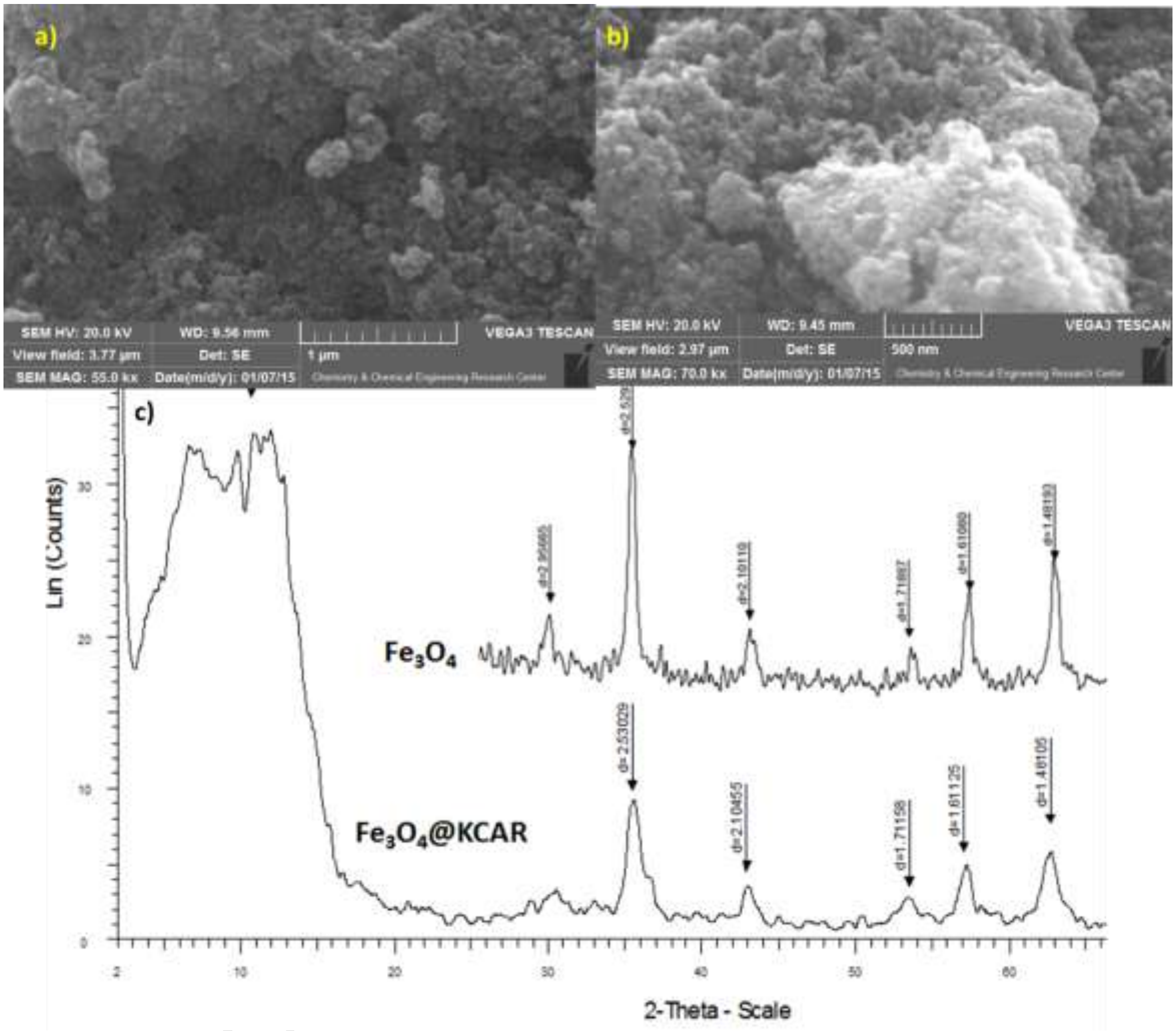


Fig. 2. SEM images of as-synthesized (a) and (b) Fe_3O_4@KCAR. X-ray diffraction pattern of Fe_3O_4@KCAR (c).

To understand the catalytic effect of Fe_3O_4@KCAR, several amount of that were added to reaction mixture of a benzyl amine, carbon disulfide and DMAD as model reaction. In this study, the reaction in the absence of Fe_3O_4@KCAR had few progress during 5-10 min. While in the presence of 0.01 g per each mmol of reaction, a remarkable amount of rhodanine was produced which proves the effective catalytic activity of Fe_3O_4@KCAR in the three-component reaction of rhodanine synthesis. In the presence of 0.02 g and 0.03 g of Fe_3O_4@KCAR, the reaction media turns to pasty and the reaction yield decreases (Figure 3a).

In this work, various solvents were tested to find a suitable solvent for this synthetic pathway. The solvent was selected based on its ability to produce a high yield while being a green and economical solvent according to twelve roles of green chemistry (Figure 3b). EtOH and H_2O had high product yield, however, H_2O is greener solvent rather to EtOH.

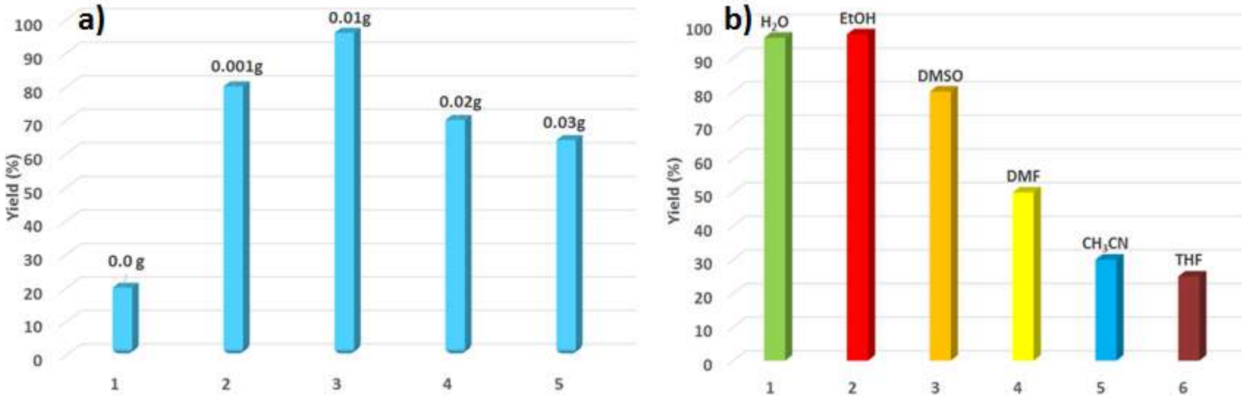
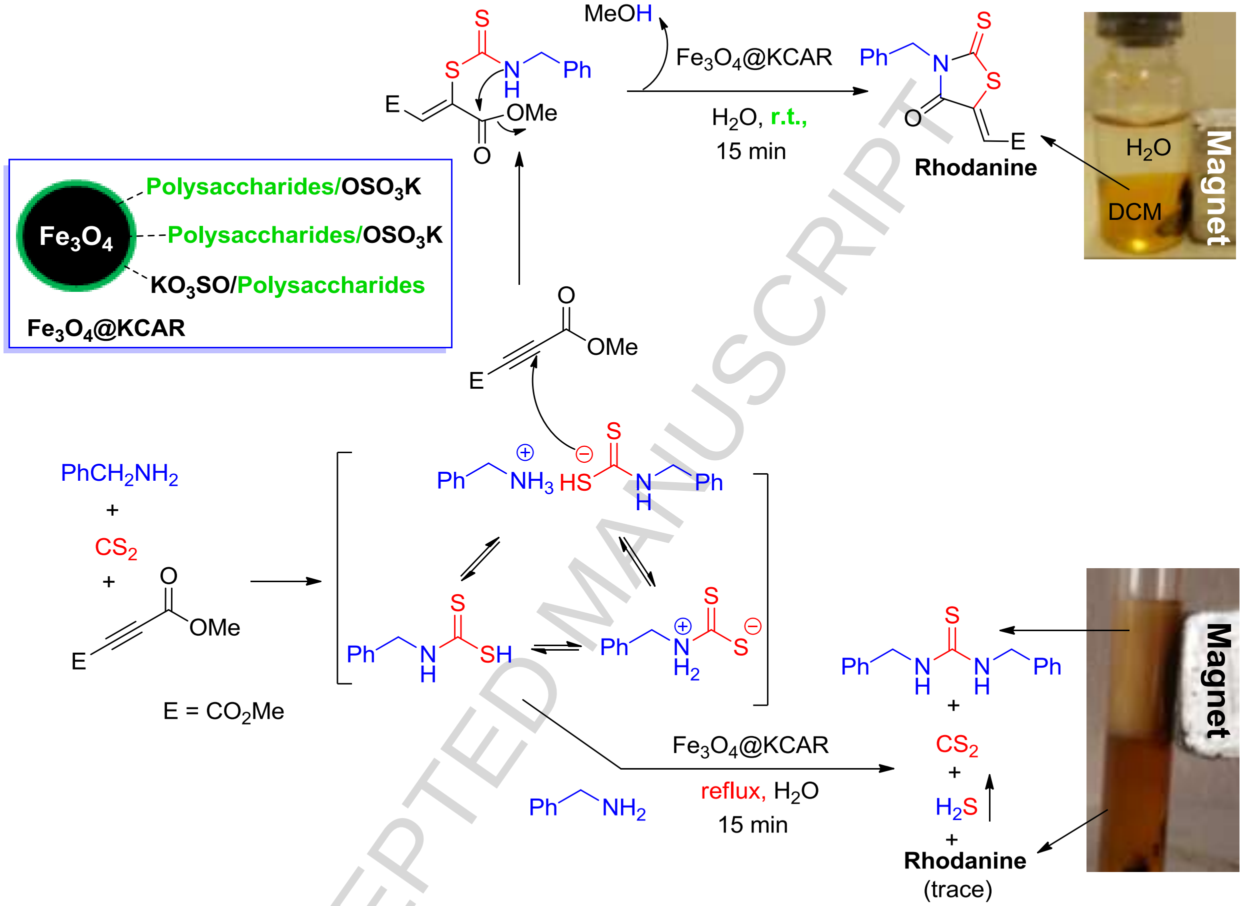


Fig. 3. a) The effect of catalyst amount. Conditions: b) The solvent effect in Fe_3O_4@KCAR accelerate. Reaction conditions: 1 mmol benzyl amine, 1 mmol CS_2, 1 mmol DMAD, and Fe_3O_4@KCAR at room temperature for 15 min.

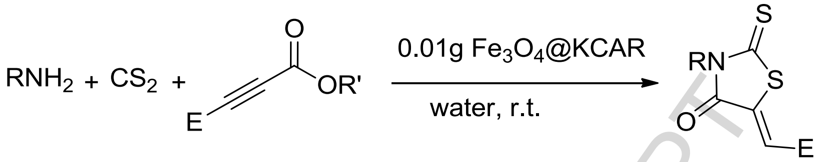
Among the several criteria, the optimum temperature was the room temperature (Scheme 2). This is due to low boiling point of CS_2 and production of side products such as thiourea (Evolution of H_2S gas indicates the formation of side products). When the reaction temperature is high, a additional amine can attack to intermediate dithiocarbamate to form thiourea.



Scheme 2. Clean synthesis of rhodanine.

Under the optimized conditions, we extended our methodology to synthesize diverse derivatives of rhodanine. In this derivatization, rhodanine-based heterocycles were synthesized in high yields and with insignificant side products. The variation of derivatives was based on changing amine and methoxy carboxylate moieties. The used amines in this work was aliphatic or benzylic which their yields had no distinctive difference.

Table 1. Synthesis of rhodanine under the catalysis of Fe_3O_4@KCAR.[a]



Entry	R	R'/E	Time (min)	Yield (%)[b]	Mp °C	
					Reported [19]	Found
1	$C_6H_5CH_2$	Me/CO_2Me	15	96	131-133	130-132
2	*p*-Cl-$C_6H_4CH_2$	Me/CO_2Me	15	95	-	115-117
3	*o*-Cl-$C_6H_4CH_2$	Me/CO_2Me	15	96	113-115	111-114
4	*o*-Cl-$C_6H_4CH_2$	Et/CO_2Et	15	94	105-109	103-106
5	$C_6H_5CH(CH_3)$	Me/CO_2Me	15	95	87-90	88-90
6	$CH_3CH(CH_3)CH_2$	Me/CO_2Me	15	95	85-90	89-90
7	CH_2=$CHCH_2$	Me/CO_2Me	15	93	139-144	141-143
8	$CH_3CH(CH_3)$	Me/CO_2Me	15	92	60-66	58-63
9	C_6H_5	Et/CO_2Et	120	-	-	-
10	*p*-Cl-C_6H_4	Me/CO_2Me	120	-	-	-

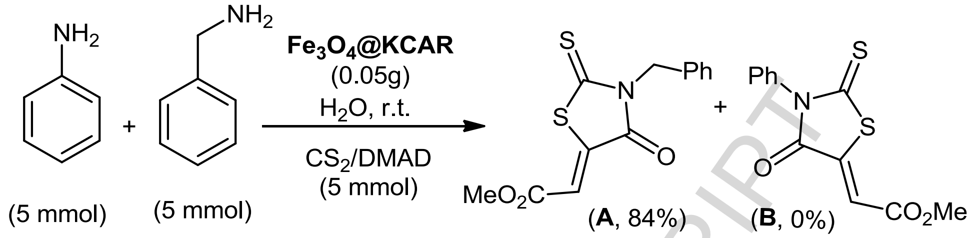
[a] Reaction conditions; 1 mmol amine, 1 mmol CS_2, 1 mmol DMAD, and 0.01 g of Fe_3O_4@KCAR in the presence of 2 ml H_2O at room temperature.

[b] Isolated yield based on DMAD.

Therefore, the synthesis of rhodanine was performed by the reaction of an amine and CS_2 to *in situ* production of dithiocarbamate and its subsequent reaction with DMAD under the aqueous conditions at room temperature for 10-15 min. The progress of reaction is represented by photography during several minutes. Also, the final step, work-up, is simply done by adding dichloromethane and an external magnet. The catalyst can be collected by the external magnet and the catalyst transfers to organic phase (Figure 4).

Fig. 4. Photograph representation of the reaction progress.

The catalytic activity of Fe_3O_4@KCAR in the domino three-component process to synthesis of rhodanine **A** and **B** was also studies under the optimized conditions. When we set the reaction with a mixture of an aromatic amine (aniline) and aliphatic amine (benzyl amine) in presence of the carbon disulfide and dimethyl acetylenedicarboxylate (DMAD), after 15 min the yield of **A** was 84% without any detected product of **B** (Scheme 3).



Scheme 3. Chemoselective synthesis of alkyl rhodanines *vs* aryl rhodanines.

Also, the recyclability of our proposed catalyst was studied in the reaction of benzylamine, CS_2 and DMAD. Results exhibited that the catalyst has recyclability in addition to its easy and simple recovery. In this study, Fe_3O_4@KCAR has ability to be recycled at least for 9 runs (Figure 5).

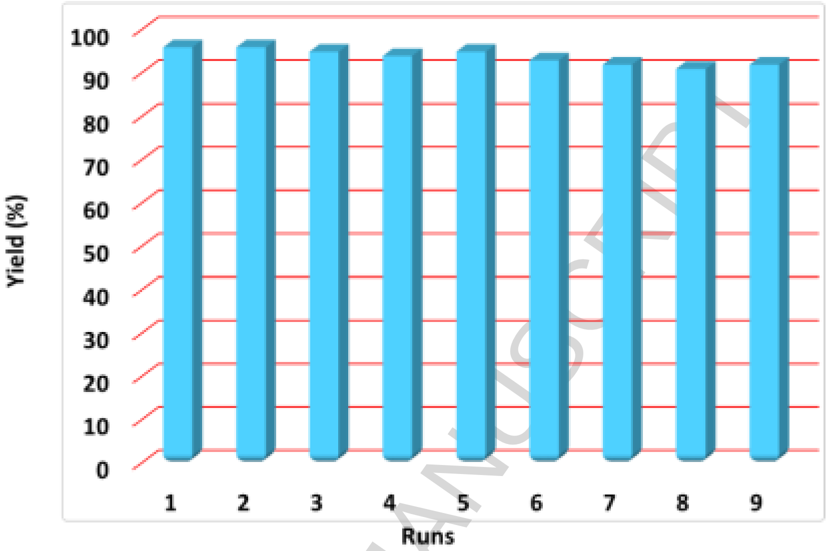


Fig. 5. Recyclability of Fe_3O_4@KCAR.

4. Conclusion

The synthesis of Fe_3O_4 in the presence of KCAR has converted it to a magnetically recoverable nanocomposite. It was concluded that Fe_3O_4@KCAR can be used as a catalyst in a multicomponent reaction with no further requirement for a post-modification step. Also, the first direct catalytic use of Fe_3O_4@KCAR nanocomposite in the catalysis was studied and reported in the three-component synthesis of rhodanine. The clean and rapid synthesis on one hand and simple work-up and product separation on the other hand were successfully achieved by biodegradable and magnetically recoverable Fe_3O_4@KCAR. Higher temperatures caused to a significant decrease in the product yield. Recyclability of Fe_3O_4@KCAR was also accomplished at least for 9 successful runs. This catalyst can have great impact on the development on the Fe3O4-KCAR catalyst and also some oncoming works about supporting catalytically active metal and even enzymes can be anticipated for this nanocomposite.

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► Fe_3O_4@KCAR nanocomposite as a nanomagnetically catalyst. ► Green synthesis of the rhodanines. ►A reusable magnetic nanocatalyst synthesis using commercially available compounds. ►Represents advantages, operational simplicity, no waste, higher yield and with easy workup.

Research highlights