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An environmentally benign and efficient synthesis of 2-thio-substituted benzothiazoles

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ABSTRACT

An environmentally benign, simple and highly efficient method for the synthesis of 2-thio-substituted benzothiazole derivatives has been achieved in good to excellent yields by reacting a series of aryl halides with 2-mercapto benzothiazole, using recyclable $CuFe_2O_4$ nanoparticles under ligand free conditions in PEG-400 as solvent. In the present protocol, the copper ferrite nanoparticles can be recovered and reused up to four cycles without significant loss of activity.

1. Introduction

In the area of heterocyclic chemistry, fused five member systems are important building blocks, and among these 2-thio-substituted benzothiazoles have been designed and synthesized for biological evaluation. 2-Thio-substituted-1,3-benzothiazoles are significant scaffolds found in a large number of pharmaceutically active molecules [1-6]. These include Cathepsin-D inhibitor, potent heat shock protein-90 inhibitor, avarol-3′-thiobenzothiazole, 2-(thiocyanatomethylthio)-1,3-benzothiazole, and dual antagonist for the human CCR1 and CCR3 receptors [7,8]. 2-Thio-substituted-1,3-benzothiazoles have also been found in advanced materials used as corrosion inhibitors and vulcanization catalysts in the rubber industry and reagents for metal-catalyzed cross-coupling reactions. Some of the biologically active 2-thio-substituted benzothiazoles are given in Figure 1. Due to the significance attached to 2-thio-substituted benzothiazoles many research groups are attracted towards exploring various ecofriendly protocols [9]. Recently green chemistry has attracted the attention of all research groups to peruse organic synthetic transformations in sustainable reaction mediums [10].

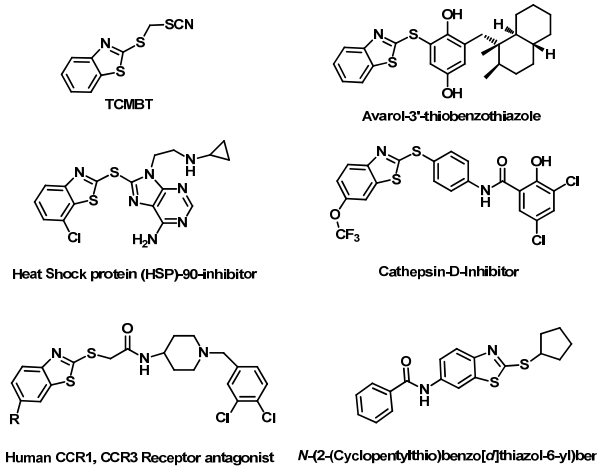

Figure 1. Biologically active *N*-substituted-2-aminobenzothiazole derivatives.

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Polyethylene glycol (PEG) is a polymerized compound of ethylene oxide, which is hydrophilic in nature. It has benign characteristic properties with respect to environment and chemical industry such as low cost, low flammability, low toxicity, recyclability, facile degradability, and miscibility with various organic solvents likes toluene, dichloromethane, alcohol, and acetone [11], compared to ionic liquids, supercritical fluids, and micellar systems [12]. Polyethylene glycol is compatible with several organic synthetic transformations like substitution reactions [13], oxidation and reduction reactions [14], Heck reaction [15], asymmetric dihydroxylation [16], Suzuki cross-coupling reaction [17], Wacker reaction [18], and partial reductions of alkynes [19].

The fascinating area of cross-coupling chemistry led many research groups to develop new catalytic systems to obtain several libraries of new molecules. Due to various applications associated with 2-thio-substituted benzothiazoles, C-S bond formation through coupling reaction using copper has been developed [20]. Recently, Wei-Yi Wu and co-workers described the synthesis of 2-thiosubstituted benzothiazole by $FeCl_3.6H_2O$ catalyzed C-S bond formation from 2-mercapto benzothiazole with corresponding aryl halide [21]. Even though, the reported methods serve the purpose of obtaining 2-thio-substituted benzothiazoles, these reported catalytic systems are not recyclable.

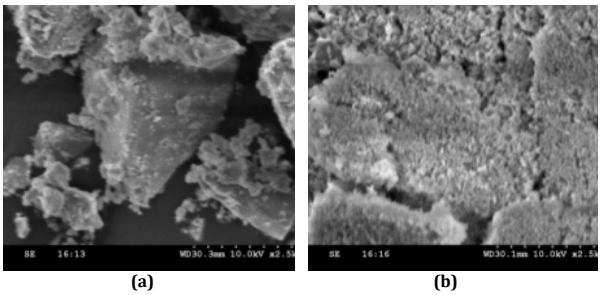
In continuation of our work in the field of cross-coupling reactions [22-30] herein, we describe an inexpensive, air-stable and recyclable nanocopper ferrite as a catalyst for the synthesis of 2-thio-substituted benzothiazoles under ligand-free conditions. Heterogeneous catalysts are useful both from economic and industrial point of view when compared to homogeneous catalysts. The high surface area and reactive morphologies of nanomaterials allow them to be effective catalysts for organic synthesis. Copper ferrite nanoparticles ($CuFe_2O_4$ nanoparticles) have the advantages of recyclability, easy workup, and cleaner reaction profiles apart from lack of nessesity of external ligands minimizing the organic waste generation as compared to the conventional catalytic systems. A mixture of 2-iodo aniline (0.5 mmol), carbon disulfide (0.6 mmol), $CuFe_2O_4$ nanoparticles (0.06 mmol), and Cs_2CO_3 (1.5 mmol) in PEG-400 (3 mL) was stirred at 90 °C for 8 h. The product 2-mercapto benzothiazole was synthesized in good to excellent yield. The results are included in Table 1. The identity and purity of the product was confirmed by ^{1}H NMR, and ESI-MS and compared with authentic samples in literature [31].

2. Experimental

All materials were purchased from Sigma Aldrich. Dry solvents, $CuFe_2O_4$ nanopowder (<50 nm) were used for the reactions. Column chromatography was carried out using silica gel (60-120 mesh size). Analytical thin layer chromatography (TLC) was carried out using silica gel 60 F_{254} pre-coated plates. Visualization was accomplished with UV lamp, I_2 stain, and phosphomolybdic acid charring. All the products were characterized by their NMR (Varian 200 or Avance 300 spectrometer) and Mass spectra (VG Autospec). ^{1}H NMR and ^{13}C NMR were recorded on 200 or 300 MHz in $CDCl_3$, and the chemical shifts were reported in parts per million (ppm, δ) downfield from the tetramethylsilane. Scanning electron microscopy (SEM) analyses were performed using a Make: Hitachi S- 3000N scanning electron microscope. Powder X-ray diffraction (XRD) analyses were performed using a Make: Bruker, Model: D8- Advance, Detector: Lynx-Eye.

2.1. Recovering of $CuFe_2O_4$ nanoparticles

The reusability of the nano copper ferrite catalyst was examined, after completion of the reaction, $CuFe_2O_4$ nano particles were allowed to be on the bottom of the flask by a neodymium magnet, and the supernatant solution was removed. The separated nano catalyst was washed successively with 10 mL of water, ethanol, ethyl acetate, dichloromethane, and hexane and then dried. No significant loss of catalyst activity was observed up to four cycles. It was observed from the SEM studies (Figure 2) that the used $CuFe_2O_4$ nanoparticles were similar in morphology, to the native catalyst even after four cycles.



(a) (b)

Figure 2. SEM images of $CuFe_2O_4$ nanoparticles (a) native $CuFe_2O_3$ nanoparticles, (b) $CuFe_2O_4$ nanoparticles after four cycles.

2.2. General procedure for the synthesis of 2-thio-substituted benzothiazole derivatives

A mixture of 2-mercapto benzothiazole (0.5 mmol), iodo benzene (0.6 mmol), $CuFe_2O_4$ nanoparticles (0.06 mmol), and Cs_2CO_3 (1.3 mmol) in PEG-400 (3 mL) was stirred at 90 °C for 8 h. After completion of the reaction, $CuFe_2O_4$ nano particles were allowed to be at the bottom of the flask by a neodymium magnet, and the supernatant solution was removed. The supernatant solution was extracted with ethyl acetate and the organic layer was washed with water and brine, and then dried over Na_2SO_4. After removal of the solvent in vacuum, the residue was purified by silica-gel chromatography to give the desired 2-thio-substituted benzothiazoles. The identity and purity of the product was confirmed by ^{1}H NMR, ^{13}C NMR and ESI-MS.

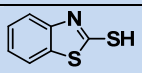
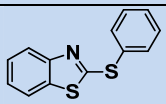
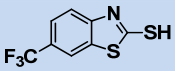
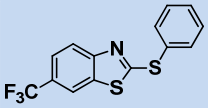
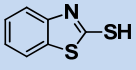
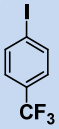
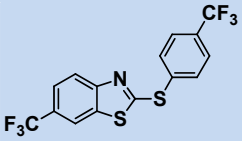
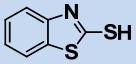
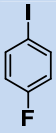
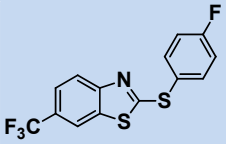
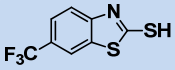
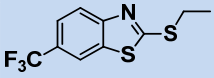
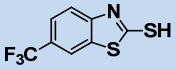
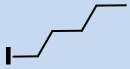
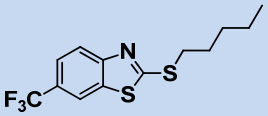
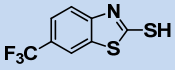
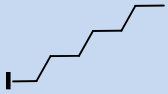
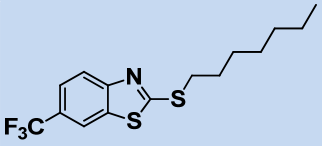
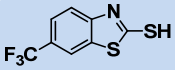
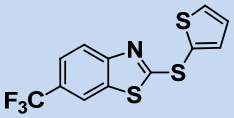
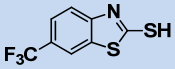
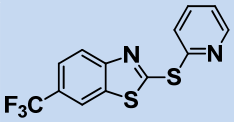
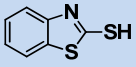
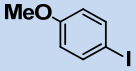
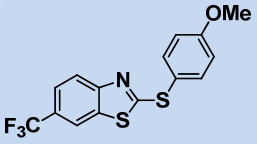
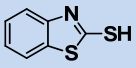
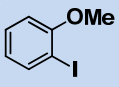
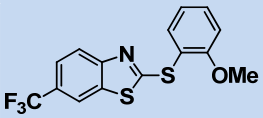
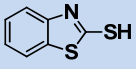
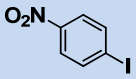
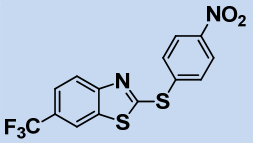
2.3. General procedure for the synthesis of 2-mercapto benzothiazole derivatives

A mixture of 2-iodo aniline (0.5 mmol), carbon disulfide (0.6 mmol), $CuFe_2O_4$ nanoparticles (0.06 mmol), and Cs_2CO_3 (1.5 mmol) in PEG-400 (3 mL) was stirred at 90 °C for 5 h. After the reaction, after completion of the reaction, $CuFe_2O_4$ nano particles were allowed to be at the bottom of the flask by a neodymium magnet, and the supernatant solution was removed. The supernatant solution was extracted with ethyl acetate and the organic layer was washed with water and brine, and then dried over Na_2SO_4. After removal of the solvent in vacuum, the residue was purified by silica-gel chromatography to give the desired substituted 2-mercapto benzothiazoles in good to excellent yields (Scheme 1).

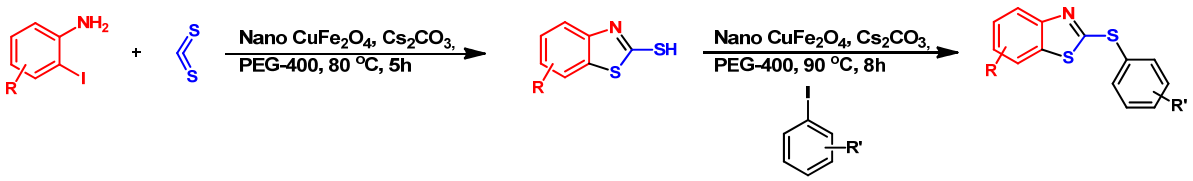
2-(Phenylthio)benzo[d]thiazole (Table 1, Entry 1, **3a**): ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm) 7.89 (d, 1H, *J* = 8.3 Hz, Ar-H), 7.79-7.72 (m, 2H, Ar-H), 7.66 (d, 1H, *J* = 8.3 Hz, Ar-H), 7.54-7.46 (m, 3H, Ar-H), 7.45-7.38 (m, 1H, Ar-H) 7.32-7.27 (m, 1H, Ar-H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 135.3, 130.4, 129.9, 126.1, 124.31, 121.9, 120.7 (Ar-C). ESI-MS (*m/z*): 244 $(M + H)^{+\cdot}$.

2-(Phenylthio)-6-(trifluoromethyl)benzo[d]thiazole (Table 1, Entry 2, **3b**): ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.66 (s, 1H, Ar-H), 7.57-7.43 (d, 1H, Ar-H), 7.30-7.23 (m, 2H, Ar-H), 7.20-7.07 (m, 3H, Ar-H), 6.81 (d, 1H, *J* = 9.0 Hz, Ar-H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 114.5 (Ar-C), 120.6 (Ar-C), 123.5 (CF_3-C), 124.3 (Ar-C), 125.9 (Ar-C), 126.7 (Ar-C), 129.1 (Ar-C), 134.5 (Ar-C), 140.4 (Ar-C), 153.9 (Ar-C). ESI-MS (*m/z*): 312 $(M + H)^{+\cdot}$.

Table 1. Synthesis of 2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one derivatives [a].

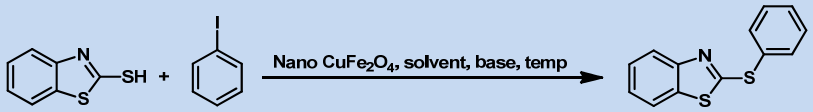
Entry	R	R'	Product	Time (h)	Yield (%) [b]
1				8	91
2				8	90
3				8	88
4				8	80
5				8	60
6				8	52
7				8	45
8				8	82
9				8	80
10				8	84
11				8	78
12				8	70

[a] Reaction conditions: A mixture of 2-mercapto benzothiazole (0.5 mmol), iodo benzene (0.6 mmol), $CuFe_2O_4$ nanoparticles (0.06 mmol), and Cs_2CO_3 (1.3 mmol) in PEG-400 (3 mL) was stirred at 90 °C for 8h.
[b] Isolated yield.



Scheme 1

Table 2. Screening of nanoparticles for the synthesis of 2-thio-substituted benzothiazoles [a].



Entry	Catalyst	Base	Solvent	Temperature (°C)	Yield (%) [b]
1	Nano $CuFe_2O_4$	Cs_2CO_3	PEG	90	91
2	Nano $CuFe_2O_4$	K_2CO_3	PEG	90	40
3	Nano $CuFe_2O_4$	Na_2CO_3	PEG	90	20
4	Nano $CuFe_2O_4$	K_3PO_4	PEG	90	40
5	Nano $CuFe_2O_4$	Cs_2CO_3	PEG	Room temperature	Trace
6	Nano $CuFe_2O_4$	Cs_2CO_3	CH_3CN	90	25
7	Nano $CuFe_2O_4$	Cs_2CO_3	Toluene	90	30
8	Nano $CuFe_2O_4$	Cs_2CO_3	THF	90	15
9	Nano $CuFe_2O_4$	Cs_2CO_3	PEG	50	20
10	Nano $CuFe_2O_4$	-	PEG	90	0 [c]
11	Nano $CuFe_2O_4$	Cs_2CO_3	H_2O	90	0
12	-	Cs_2CO_3	PEG	90	0 [d]
13	Nano Y_2O_3	Cs_2CO_3	PEG	50	15
14	Nano NiO	Cs_2CO_3	PEG	50	10
15	Nano Co_3O_4	Cs_2CO_3	PEG	50	Trace
16	Nano $NiFe_2O_4$	Cs_2CO_3	PEG	50	13

[a] Reaction conditions: A mixture of 2-mercapto benzothiazole (0.5 mmol), iodo benzene (0.6 mmol), $CuFe_2O_4$ nanoparticles (0.06 mmol), and Cs_2CO_3 (1.3 mmol) in PEG-400 (3 mL) was stirred at 90 °C for 8 h.
[b] Isolated yield.
[c] In absence of the catalyst.
[d] In absence of the base.

2-((4-(Trifluoromethyl)phenyl)thio)benzo[d]thiazole (Table 1, Entry 3, **3c**): ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.91 (d, 1H, *J* = 7.9 Hz, Ar-H), 7.90-7.79 (d, 2H, Ar-H), 7.78-7.66 (m, 2H, Ar-H), 7.55-7.42 (m, 2H, Ar-H) 7.41-7.32 (m, 1H, Ar-H). ESI-MS (*m/z*): 312 $(M + H)^{+\cdot}$.

2-((4-Fluorophenyl)thio)benzo[d]thiazole (Table 1, Entry 4, **3d**): ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 9.03 (s, 1H, Ar-H), 8.15 (d, 2H, *J* = 8.3 Hz, Ar-H), 7.98 (d, 2H, *J* = 7.5 Hz, Ar-H), 7.64-7.43 (m, 3H, Ar-H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 163.8 (Ar-C), 151.3, F-C, 135.6 (Ar-C), 126.1 (Ar-C), 125.5 (Ar-C), 123.5 (Ar-C), 121.8 (Ar-C). ESI-MS (*m/z*): 262 $(M + H)^{+\cdot}$.

2-(Ethylthio)-6-(trifluoromethyl)benzo[d]thiazole (Table 1, Entry 5, **3e**): ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 8.03 (s, 1H, Ar-H), 7.92 (d, 1H, *J* = 8.3 Hz, Ar-H), 7.64 (d, 1H, *J* = 9.0 Hz, Ar-H), 3.58-3.22 (m, 2H, CH_2), 1.60-1.39 (t, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 170.8 (Ar-C), 155.2 (Ar-C), 135.1 (Ar-C), 125.8 (Ar-C), 122.9 (Ar-C), 121.3 (Ar-C), 118.4 (Ar-C), 27.8, Ali-C, 14.3, Ali-C.
ESI-MS (*m/z*): 264 $(M + H)^{+\cdot}$.

2-(Pentylthio)-6-(trifluoromethyl)benzo[d]thiazole (Table 1, Entry 6, **3f**): ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 8.09-8.01 (s, 1H, Ar-H), 8.95-8.90 (d, 1H, Ar-H), 7.69-7.55 (d, 1H, Ar-H), 3.45-3.28 (t, 2H, CH_2), 1.87-1.70 (m, 6H, CH_2), 0.93-0.83 (s, 3H, CH_3). ESI-MS (*m/z*): 306 $(M + H)^{+\cdot}$.

2-(Heptylthio)-6-(trifluoromethyl)benzo[d]thiazole (Table 1, Entry 7, **3g**): ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 8.03 (s, 1H, Ar-H), 7.92 (d, 1H, *J* = 8.4 Hz, Ar-H), 7.77-7.69 (d, 1H, Ar-H), 3.48-3.28 (t, 2H, CH_2), 1.99-1.75 (m, 2H, CH_2), 1.40-1.20 (m, 8H, CH_2), 0.97-0.78 (m, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 171.2 (Ar-C), 155.3 (Ar-C), 135.2 (Ar-C), 123.1 (Ar-C), 121.4 (Ar-C), 118.4 (Ar-C), 33.6, Ali-C, 31.6, Ali-C, 29.0, Ali-C, 28.7, Ali-C, 22.5, Ali-C, 14.0, Ali-C. ESI-MS (*m/z*): 334 $(M + H)^{+\cdot}$.

2-(Thiophen-2-ylthio)-6-(trifluoromethyl)benzo[d]thiazole (Table 1, Entry 8, **3h**): ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 8.15-8.00 (m, 1H, Ar-H), 7.97-7.90 (m, 1H, Ar-H), 7.73-7.69 (m, 1H, Ar-H), 7.65 (d, 1H, *J* = 8.3 Hz, Ar-H), 7.35-7.30 (m, 1H, Ar-H), 7.23-7.18 (m, 1H, Ar-H). ESI-MS (*m/z*): 317 $(M + H)^{+\cdot}$.

2-(Pyridin-2-ylthio)-6-(trifluoromethyl)benzo[d]thiazole (Table 1, Entry 9, **3i**): ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 8.42-8.35 (m, 2H, Ar-H), 7.77-7.70 (d, 2H, Ar-H), 7.37-7.32 (m, 1H, Ar-H), 7.31-7.28 (m, 2H, Ar-H). ESI-MS (*m/z*): 313 $(M + H)^{+\cdot}$.

2-((4-Methoxyphenyl)thio)-6-(trifluoromethyl)benzo[d] thiazole (Table 1, Entry 10, **3j**): ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.17-7.05 (m, 2H, Ar-H), 6.88-6.70 (m, 4H, Ar-H), 6.66-6.55 (m, 1H, Ar-H), 3.66 (s, 3H, OCH_3). ESI-MS (*m/z*): 342 $(M + H)^{+\cdot}$.

6-(Trifluoromethyl)benzo[d]thiazole-2-thiol (Intermediate, **A1**): ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 11.08-10.88 (m, 1H, S-H), 7.77-7.72 (s, 1H, Ar-H), 7.67-7.59 (d, 1H, Ar-H), 7.39-7.32 (d, 1H, Ar-H). ESI-MS (*m/z*): 235 $(M + H)^{+\cdot}$.

3. Results and discussion

Initially, 2-mercapto benzothiazole and iodobenzene were used as model reactants to optimize the reaction conditions such as bases, solvents, and reaction temperature (Table 2). Among, several bases screened, Cs_2CO_3 was found to be an excellent base (Table 2, Entry 1). In the presence of bases such as K_2CO_3, Na_2CO_3, and K_3PO_4, lesser amount of the desired product was obtained (Table 2, Entry 2, 3, 4).

The effect of solvents was also investigated and the highest yield was observed in PEG-400 (polyethylene glycol), while reaction in solvents such as THF, CH_3CN and toluene resulted in moderate yields. The experiment confirmed that the reaction

did not occur in the absence the base (Table 2, Entry 10). Different nano catalysts were screened in this protocol (Table 2, Entries 13-16). When the reaction was conducted at room temperature trace amount of desired product were obtained (Table 2, Entry 5). Ideal temperature for the reaction was found to be 90 °C. The influence of the amount of catalyst on the yield of the product was also evaluated. It was observed that 0.06 mmol of nano $CuFe_2O_4$ was ideal for synthesis of 2-thio-substituted benzothiazoles under ligand-free conditions.

The reusability of the nano copper ferrite catalyst was examined and the results are summarized in Figure 3.

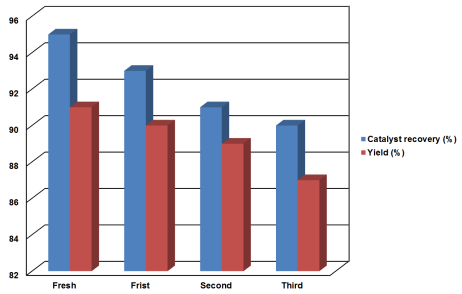


Figure 3. Recycling of $CuFe_2O_4$ nanoparticles (Reaction conditions: A mixture of 2-mercapto benzothiazole (0.5 mmol), iodo benzene (0.6 mmol), $CuFe_2O_4$ nanoparticles (0.06 mmol), and Cs_2CO_3 (1.3 mmol) in PEG-400 (3 mL) was stirred at 90 °C for 8 h).

After completion of the reaction, $CuFe_2O_4$ nano particles were allowed to be at the bottom of the flask by a neodymium magnet, and the supernatant solution was removed. The separated nano catalyst was washed successively with 10 mL of water, ethanol, ethyl acetate, dichloromethane, and hexane and then dried. No significant loss of catalyst activity was observed up to four cycles. The native and used $CuFe_2O_4$ nanoparticles were analyzed by powder XRD and SEM analysis. The SEM studies showed that the morphology of $CuFe_2O_4$ was almost similar in both before and after the reaction conditions. The powder XRD spectra (Figure 4 and 5) also confirmed the intactness of the particles after four cycles (supporting. information).

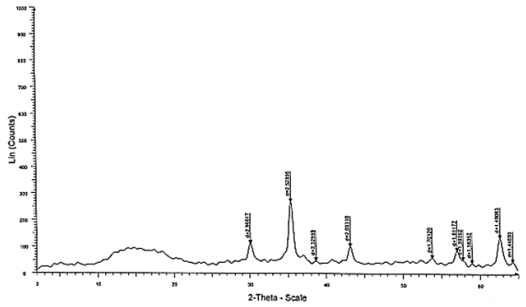


Figure 4. Powder XRD - images of Native $CuFe_2O_4$ nanoparticles.

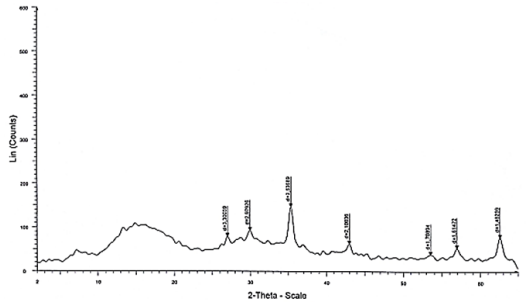


Figure 5. Powder XRD - images of $CuFe_2O_4$ nanoparticles after four cycles.

5. Conclusion

A simple and green protocol was developed for the synthesis of 2-thio-substituted benzothiazoles using recyclable $CuFe_2O_4$ nanoparticles under ligand free conditions in an eco-friendly PEG-400 solvent.

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