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*Article*

# Cellulose@$Fe_2O_3$-$SO_3H$: A Novel Magnetic Composite Nanomaterial for the Synthesis of Chromene Derivatives

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**Abstract:** Magnetic nanocomposites are one of the best catalysts for organic reaction because of their simple recoverable features. We can simply recover these catalysts from reaction pot with one external magnetic field. A possible method simple separation and recycling of the catalysts is immobilizing catalytically active species in the surface of magnetic particles which can be separated from the reaction system by applying an appropriate magnetic field. Cellulose, as an important and naturally abundant biopolymer, can be easily functionalized with various organic groups for desired purposes like applications as a support for heterogeneous catalysis, composites matrixes and immobilization processes.

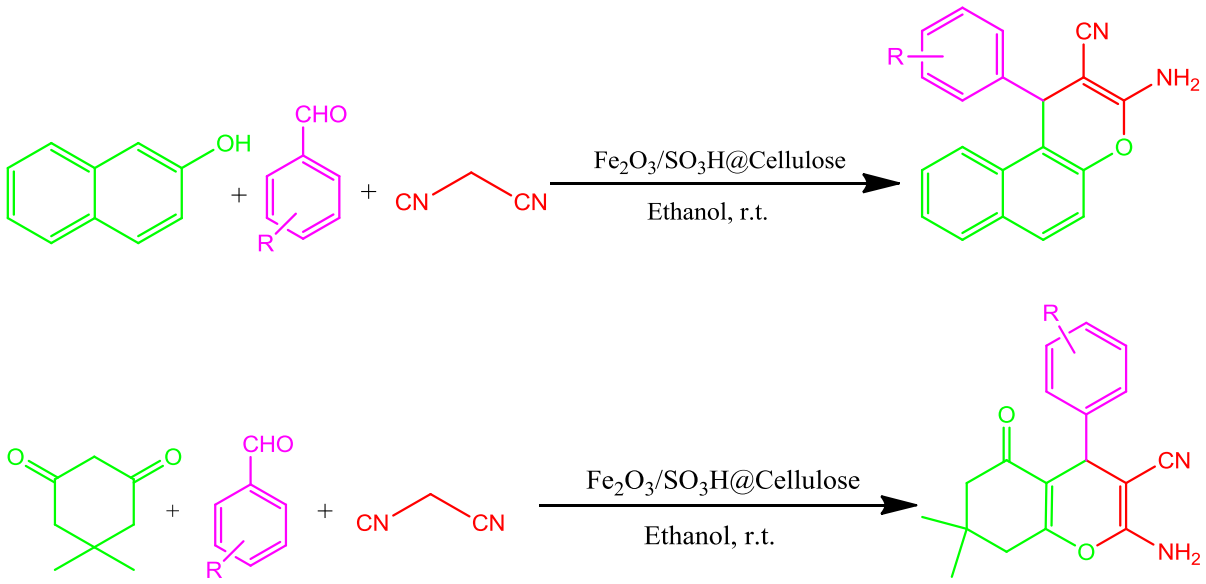
In this study, we have prepared a biopolymer-based magnetic nanocomposite via in situ synthesis of maghemite (gamma-$Fe_2O_3$) on cellulose and then its sulfonation. It has been proven that sulfonated catalyst shows very good activities for one-pot three-component synthesis of chromenes under mild reaction conditions. In general this catalyst is recoverable, green, easy separation because of its magnetic feature, environmentally friendly properties and good yield and low reaction time for this multicomponent reaction as a very good strategy for the synthesis of medicinal and pharmaceutical compounds.

**Keywords:** Nanocomposite, Cellulose, $Fe_2O_3$, Chromene, Catalyst, Magnetic nanoparticles.

## 1. Introduction

Chromenes are an important class of compounds belonging to the flavonoid group that occur naturally in fruits, vegetables, nuts, seeds, flowers, and barks [1–3], They are an integral part of the human diet and have been reported to exhibit a wide range of biological effects [4–11]. They also demonstrate antioxidant [12], anti-inflammatory [13], antibacterial [14] and antitumor properties [15]. 2-Amino-chromenes represent an important class of compounds being the main components of many naturally occurring products, and have been of interest in recent years due to their useful biological and pharmacological aspects [16], The most straightforward synthesis of this heterocyclic system involves a three-component coupling of aromatic aldehyde, malononitrile and oxygen containing systems such as dimedone, cyclohexadion, 1-naphtol and 2-naphtol. Traditionally, this reaction was catalyzed by a basic catalyst such as piperidine [17]. Many homogeneous catalysts have been employed for this condensation including ammonium salts [18], NaOH [19], $K_2CO_3$ [20], $I_2/K_2CO_3$ [21], $TiCl_4$ [22], $InCl_3$ [23], heteropolyacid [24] and $Et_3N$ [25]. Most of these catalysts have disadvantages such as low yield and long reaction time. In present study we wish to report a high yield and effective synthesis of chromones by use of gamma-$Fe_2O_3/SO_3H$ as a heterogeneous catalyst (Scheme 1).

**Sheme 1.** Synthesis of 2-Amino-4H-chromen derivatives.



## 2. Results and Discussions

The synthesis reaction of 2-amino-4H-chromen derivatives can be done by combination of dimedone, cyclohexandion, 1-naphtol , 2-naphtol with aromatic aldehyde and malononytrile. Reaction screening in various condition shows that solvent should be ethanol and optimize amount of starting material is 1 mmol 1-naphtol,1 mmol malononytrile,1 mmol 3-nitrobenzaldehyde in the peresence of 0.01g catalyst gamma-$Fe_2O_3$/$SO_3H$@cellulose. After a few minutes monitoring by TLC shows that reaction is complete. After optimazation of condition, reaction was done by various oxygen sources as we mentioned them above. The result are shown in following table.in order to optimazation of catalyst amount we use the facts on table 1. Obtained data shows that optimazation amount of catalyst for this reaction is 0.08 g.

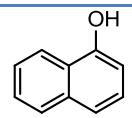
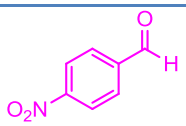
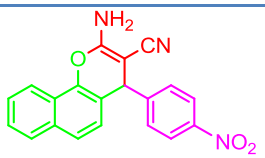
**Table 1.** Optimization of the catalyst amount for the Synthesis 2-amino-4-(3-nitrophenyl)-4H-benzo[h]chromen-3-carbonitrile.[a]

| Entry | Catalyst amount (g) | Time (min) | Isolated yield (%) |
|---|---|---|---|
| 1 | 0 | 120 | trace |
| 2 | 0.02 | 8 | 60 |
| 3 | 0.06 | 8 | 85 |
| 4 | 0.08 | 8 | 99 |
| 5 | 0.1 | 8 | 99 |

[a] Conditions: 1 mmol 3-nitrobenzaldehyde, 1 mmol malononitrile, 1 mmol 1-naphtol, 3 mL ethanol, gamma-$Fe_2O_3$/$SO_3H$@cellulose.

The scope and generality of synthesis of 2-amino-4H-chromen derivatives are well showed with structurally diverse benzaldehyde and oxygen source. The results are summarized in Table 2.

**Table 2.** Synthesis of 2-amino-4H-chromen derivatives in the presence of gamma-$Fe_2O_3$/$SO_3H$@cellulose.

| Entry | O source | RCHO | Product | Time (min) | Yield (%) | Mp (obsd) ($^oC$) | Mp (Lit.) ($^oC$) |
|---|---|---|---|---|---|---|---|
| 1 |  |  |  | 8 | 99 | 250-252 | 250-252 [26] |

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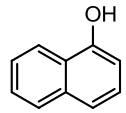
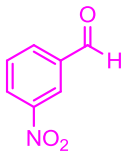
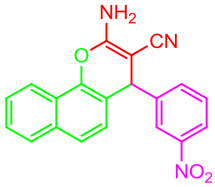
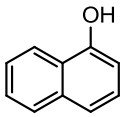
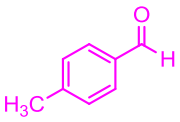
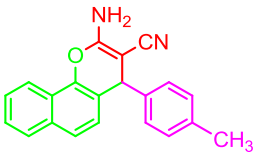
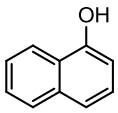
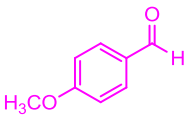
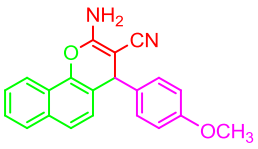
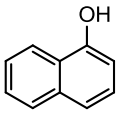
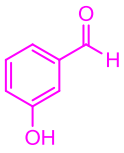
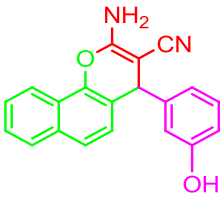
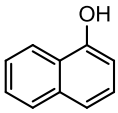
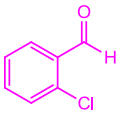
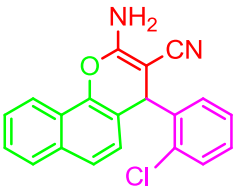
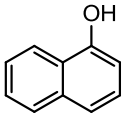
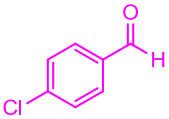
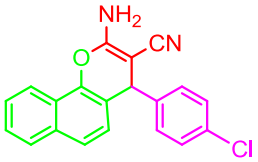
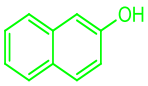
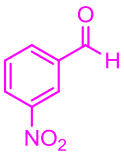
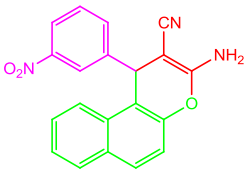
|---|---|---|---|---|---|---|---|
| 2 |  |  |  | 8 | 99 | 264-265 | 264-266[27] |
| 3 |  |  |  | 11 | 91 | 256-258 | 253-255[28] |
| 4 |  |  |  | 13 | 93 | 233-235 | 233-236[29] |
| 5 |  |  |  | 13 | 97 | 226-228 | 228-232[30] |
| 6 |  |  |  | 10 | 95 | 234-236 | 235-238[31] |
| 7 |  |  |  | 9 | 97 | 264-266 | 264-266[32] |
| 8 |  |  |  | 8 | 98 | 235-237 | 235-237[33] |

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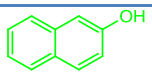
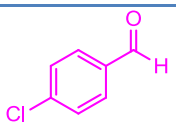
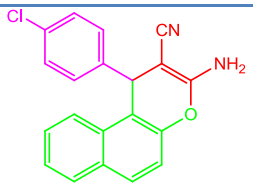
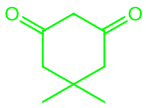
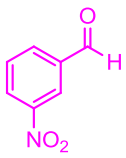
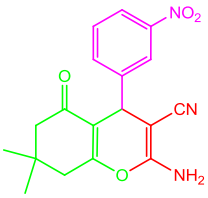
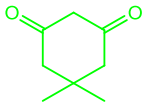
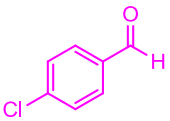
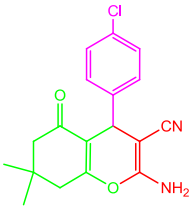
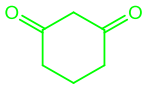
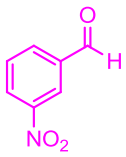
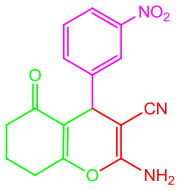
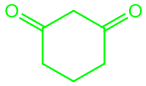
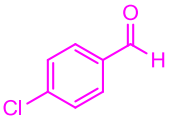
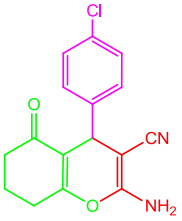
| 9 |  |  |  | 9 | 96 | 206-208 | 205-206[33] |
| 10 |  |  |  | 25 | 95 | 210-212 | 210-212[34] |
| 11 |  |  |  | 27 | 96 | 200-202 | 202-203[35] |
| 12 |  |  |  | 23 | 95 | 202-204 | 202-203[36] |
| 13 |  |  |  | 24 | 95 | 224-226 | 225-227[37] |

## 3. Experimental

### *3.1. Materials and methods*

All chemicals were purchased from Merck, Fluka and Sigma-Aldrich companies and were used without further purification. All reactions and the purity of 2-amino-4H-chromen derivatives were monitored by thin-layer chromatography (TLC) using aluminum plates coated with silica gel F254 plates (Merck) using ethyl acetate and *n*-hexane as eluents. Melting points were determined in open capillaries using an Electro thermal 9100 instrument.

### *3.2. Synthesis of gamma-$Fe_2O_3$/$SO_3H$@cellulose*

The cellulose microcrystal (5.00 g) was added to 20 mL $CHCl_3$ and stirred under vigorus magnettic. 1.00 g chlorosulfonic acid was added dropwise at 0 $^oC$ during 2h. When addition was complete, the mixture was stirred for 2 h until HCl was removed from reaction vessel. Then, the

solution was filtered and washed with methanol (3*10 mL) and dried at room temperature to afford cellulose sulfuric acid as white powder.

Aqueouse solution from NaOH, urea and $H_2O$ is prepared with material ratio 7:12:81 respectively and that's temperature is decreased to -12 $^0$C by ice and salt, and then 4.0 g cellulose sulforic acid was synthesized in the previous step dissolve directly in it. Then, 0.5 g $FeCl_2.4H_2O$ and 1.0 g $FeCl_3$. $6H_2O$ was dissolved in 50 mL deionized water and then dropwise added to cellulose sulforic acid solution, hereby gamma-$Fe_2O_3$ insitu synthesis on cellulose fiber. Thus the gamma-$Fe_2O_3$/$SO_3H$@Cellulose which is a new nanocomposite was synthesized.

*3.4. General procedure for the synthesis of 2-amino-4H-chromen derivatives.*

First, gamma-$Fe_2O_3$/$SO_3H$@cellulose (0.08 g) was added to a solution of 1-naphtol (1 mmol), malononytrile (1 mmol) and benzaldehyde (1 mmol) in 3mL of ethanol under room temprature for 8-10 min. After completion of reaction, as indicated by TLC (ethyl acetate/n-hexane 1/2), the catalyst was removed by magnet then washed with acetone and after drying could be ready to use for the next reaction without loss in activity. The crude product was filtered and recrystallized from ethanol to give products in good to high yields.

## 4. Conclusion

In summary, we introduced a new nanocomposite system based on cellulose which due to the presence gamma-$Fe_2O_3$ and $SO_3H$ has very good catalytic activity. On the other, the magnetic properties help us to separate it from reaction pot, simply. In the present work, we used this system for synthesis of 2-amino-4H-chromen derivatives in high yield and very mild conditions.

## Acknowledgements

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## Conflicts of Interest

The authors declare no conflict of interest.

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