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Nanocomposite of Fe_3O_4/Cellulose/Vitamin C as a New Biopolymer Catalyst for Synthesis of 1-(α-aminoalkyl) Naphthols, Betti Bases

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ABSTRACT

In this letter we report the synthesis of cellulose and vitamin C coated magnetite nanoparticles (MNPs) as a green catalyst for the synthesis of pharmacologically active 1-(α-aminoalkyl) Naphthols via a one-pot condensation of 2-naphthol, alkylamines and aldehydes under solvent-free conditions. The XRD results confirmed the pure magnetite phase for the prepared MNPs. Morphological observations of the prepared MNPs through SEM and TEM exhibited the uniform particle morphology with 15 nm in size. IR analysis presented all vibrations related to chemical bounds in the cellulose and vitamin C. TG analysis exhibits 12% vitamin C and 18% cellulose in MNPs composition. Magnetic analysis via VSM proved the superparamagnetic nature of the prepared MNPs.

Keywords: betti base, vitamin c, Fe_3O_4, cellulose, (α-aminoalkyl) naphthol

INTRODUCTION

One of the important reactions in the field of multicomponent synthesis is the Betti reaction which was discovered at the beginning of the 20th century by Mario Betti [1-3]. The Betti base belong to the category of 1,3-amino-oxygenated functional group compounds which comprise varieties of biologically important natural products and potent drugs [4]. Two very important such compounds are ritonavir and lopinavir being HIV protease inhibitors of great significance [5]. The 1-aminoalkyl naphthols also exhibit biological activities like hypotensive and bradycardiac effect [6]. In addition, such 1-aminoalkyl alcohol type ligands have been utilized for asymmetric synthesis where it acts as a catalyst [7]. Optically active Betti bases can be used as ligands to chelate with organometallic reagents in different reactions to provide highly efficient asymmetric induction [8-13]. Reaction of Betti bases with aldehydes produces 1,3-oxazines, an important biologically active scaffold [14,15]. The alkyl derivative of Betti base has been prepared by the original Betti procedure [16]. Thus, due to importance of ,(α-aminoalkyl) naphthol in bioorganic and pharmaceutical chemistry, design and development of simple high-yielding and environmental friendly methods by using new catalysts is of prime importance. Therefore, magnetic nanocomposites based on cellulose can be regarded as a green and efficient recoverable and biodegradable nanocatalyst [17]. In this letter, ascorbic acid -functionalized cellulose-coated Fe3O4 nanoparticles (Fe_3O_4/cellulose/ vitamin C) is introduced. Herein, in continuation of our previous works on one-pot multicomponent reaction in organic synthesis [18-20]. Fe_3O_4/cellulose/ vitamin C as a nontoxic and environmentally-friendly heterogeneous nanocatalyst was used in the synthesis of, (α-aminoalkyl) naphthol derivatives via an one-pot multicomponent reaction of 2-naphthol, alkylamines and aldehydes under solvent-free conditions at room temperature (**Scheme 1**). To the best of our knowledge, this is the first report on the application of the present composite nanostructures in the synthesis of, (α-aminoalkyl) naphthol derivatives.

Furthermore, this work includes several advantages such as green reaction media, easy work-up procedures, high surface area, activity and recyclability of the nanocatalyst. Fe_3O_4/cellulose/ vitamin C could be separated easily from the reaction mixture by using an external magnet and can be reused several times.

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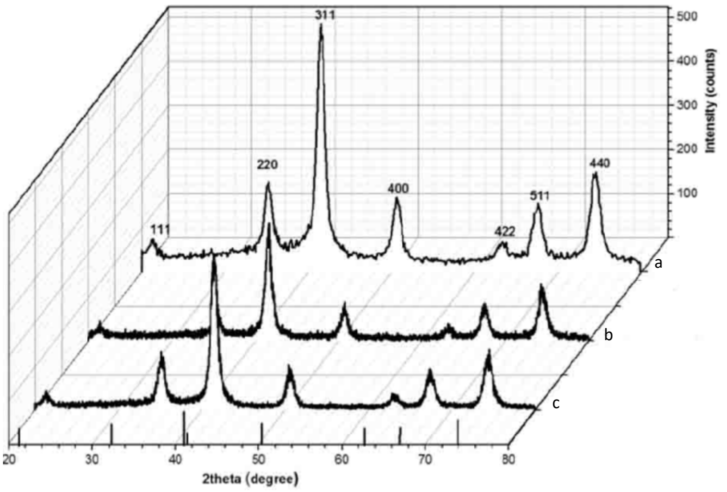


Figure 1. XRD patterns of (a) Fe_3O_4, (b) cellulose and (c) ascorbic acid coated Fe_3O_4NPs.

EXPERIMENTAL PROCEDURE

Instruments

Melting points were measured using the capillary tube method with an electro thermal 9200 apparatus (Bibby, France). SEM and TEM images were provided by TESCAN VEGA3 and Phillips EM 208 instruments. XRD patterns were recorded through a Phillips PW-1800 diffractometer with Co Kα radiation (λ = 1.789 Å). Thermogravimetric analysis was performed using a thermoanalyzer (STA-1500) at 25–600 ºC. FTIR spectra were obtained using a Bruker Vector 22 Fourier transformed infrared spectroscope. Magnetic property of the prepared NPs was measured from -20,000 to 20,000 Oe at room temperature using a Lakeshore model 7410 vibrational sample magnetometer (VSM).

Preparation of Fe3O4 / Cellulose / Vitamin C Nanocatalyst

Cellulose was dissolved directly in the NaOH/urea aqueous solution, which was precooled to -12 ºC, to prepare a transparent 4 wt % cellulose solution according to previous method [18]. Next, an aqueous solution of 0.3 g of FeCl2.4H2O and 0.8 g of FeCl3.6H2O in 100 mL of water was added dropwise to the solution to form Fe3O4@cellulose microcrystals. After that, 5.0 g of the microcrystals were added to 20 mL of chloroform and stirred vigorously. Then, ascorbic acid (1.0 g) was added dropwise at 0 °C during 2 h. When addition was completed, the mixture was stirred for 2 h and brown powder washed with methanol and dried at room temperature to yield the Fe3O4/cellulose/ vitamin C nanocatalyst (**Figure 4**).

Preparation of 1-(α-aminoalkyl)-2-naphthols: General Procedure

A mixture of 2-naphthol (1mmol), amines (1mmol) and aldehydes (1 mmol) were taken in the present of Fe3O4/cellulose/ vitamin C nanocatalyst in a round-bottomed flask and stirred at 900 rpm at room temperature for 30 min. Similarly, the same reactions were also refluxed at 80 ºC for 2 hours. Upon completion of the reaction, the solid crude products obtained were filtered, washed with water and dried in vacuum. The condensation products were isolated in excellent yields in essentially pure form after crystallization from ethanol.

RESULTS AND DISCUSSION

The XRD patterns of the prepared Fe_3O_4/cellulose/ vitamin C are shown in **Figure 1**. All diffraction peaks i.e. (111), (220), (311), (222), (400), (422), (511) and (440) observed in these patterns are fully matched with spinel magnetite phase of iron oxide (JCPD 01-088-0315). The average crystallite size (D) of the prepared NPs was calculated using Scherrer's relation (D = 0.9k/b cos (h)) to be 9.4, 8.1 and 7.6 nm, respectively. SEM and TEM images are shown in **Figure 2**, which exhibit the particle morphology for the prepared samples. It is clearly observed that both coated samples have well-defined particle shape and no obvious aggregation is observed and have mean size of 8 nm.

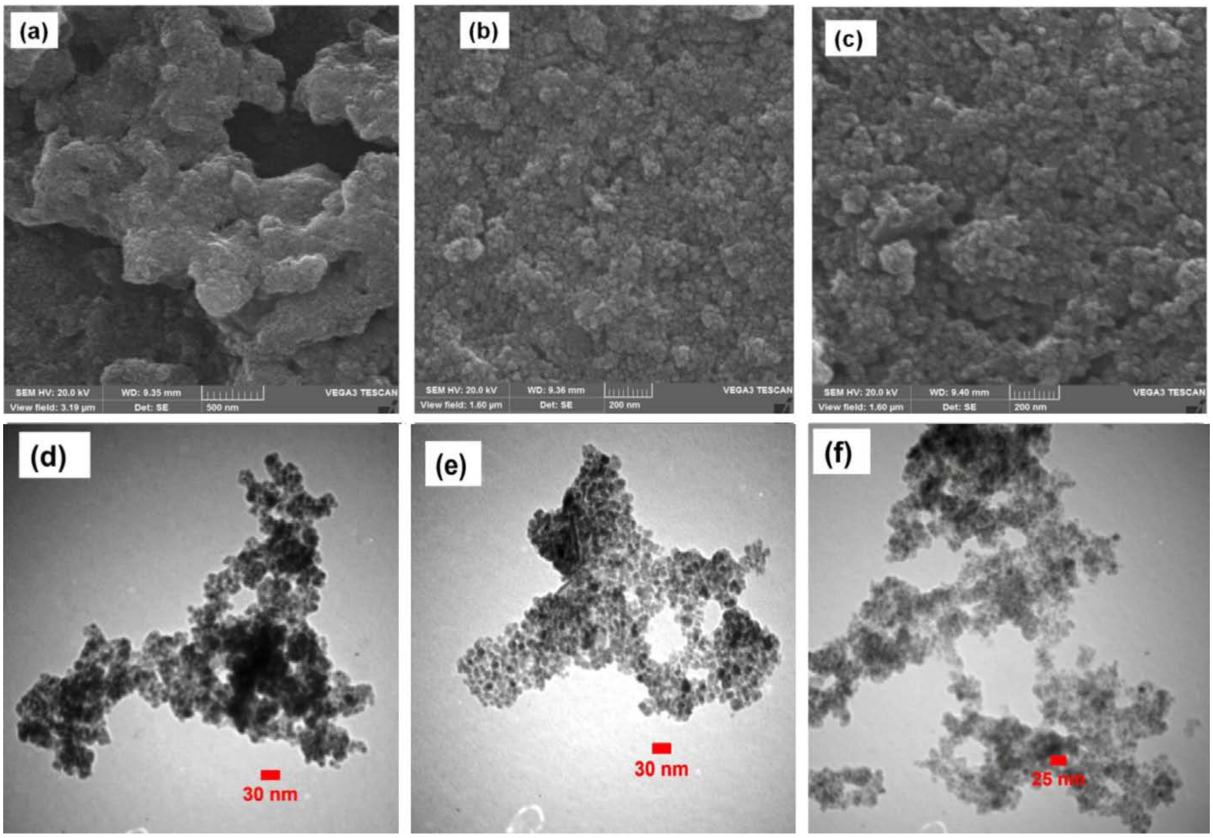


Figure 2. SEM and TEM images of the (a, d) MNPs, (b, e) cellulose and (c, f) vitamin C coated MNPs.

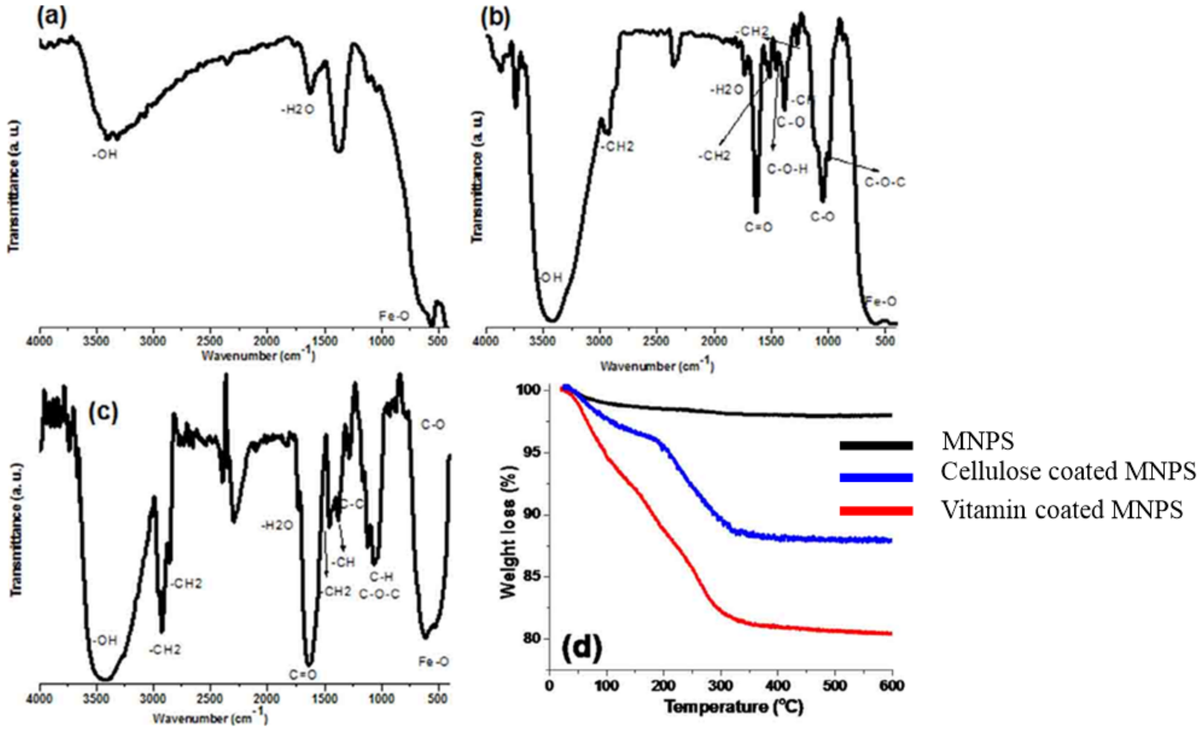


Figure 3. IR spectra of (a) MNPs (b) cellulose (c) vitamin C coated MNPs, and (d) thermogravimetric profiles of the prepared MNPs at the temperature range of 25–600 C.

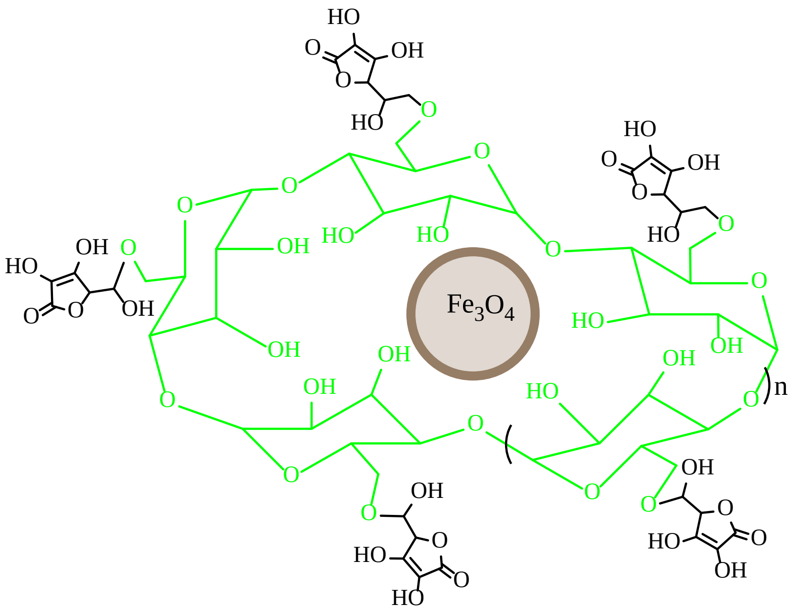
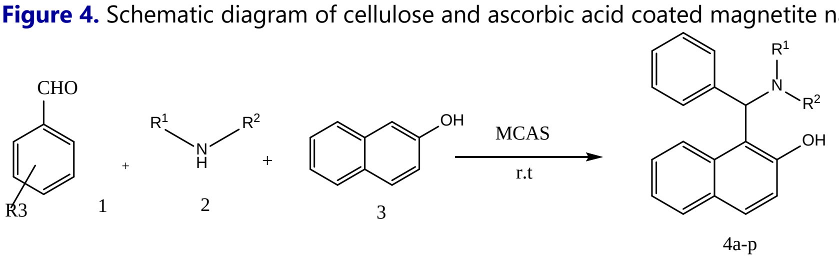


Figure 4. Schematic diagram of cellulose and ascorbic acid coated magnetite nanoparticles (MCAS).



Scheme 1. Synthesis of Betti base

Table 1. Optimizing of the model reaction conditions under solvent-free conditions at r.t.

Entry	Catalyst	Catalyst amount (mg)	Time (min)	Yield[a] (%)
1	-	-	120	15
2	Fe3O4/cellulose/vitamin C	10	80	70
3	Fe3O4/cellulose/vitamin C	20	60	65
4	Fe3O4/cellulose/vitamin C	30	20	95
5	Fe3O4/cellulose/vitamin C	40	20	80
6	vitamin C	30	80	65
7	Fe3O4/cellulose	30	60	50

[a] Isolated yields

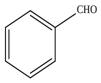
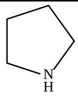
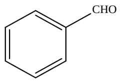
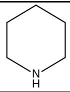
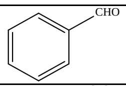
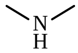
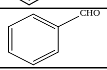
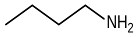
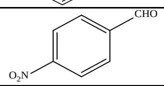
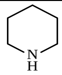
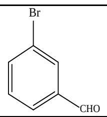
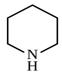
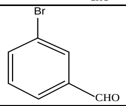
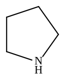
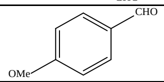
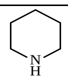
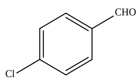
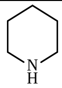
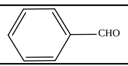
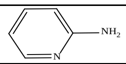
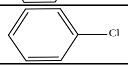
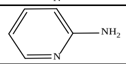
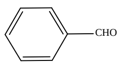
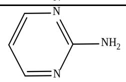
Table 2. Optimizing of the solvent and temperature in the presence of 0.03 g of Fe3O4/cellulose/ vitamin C

Entry	Solvent	Temperature(°C)	Yield (%)[a]
1	Solvent-free	50	85
2	Ethanol	50	66
3	Water	50	43
4	Solvent-free	30	90
5	Solvent-free	25	95

[a] Isolated yields after 20 min.

To optimize the reaction conditions, a pilot reaction for the synthesis of 1-(α-aminoalkyl) naphthol (4d) was carried out. The effects of the amount of the nanocatalyst, solvents and the reaction temperature were studied on the pilot reaction (Tables 1 and 2). First, we studied the effect of different amounts of Fe3O4/cellulose/ vitamin C nanocomposites. 0.03 g of Fe3O4/cellulose/ vitamin C represented the highest yields (95%) under solvent-free conditions at room temperature after 20 min (Table 1, entry 4). As can be seen in Table 1, we have also investigated various components of the catalyst as the catalyst in the pilot reaction.

Table 3. Synthesis of Betti bases in in solvent free condition

Entry	Aldehyde	Amine	Product	Time (h)	Yield	Obs. mp ºC	Lit. mp ºC
1			4a	30	92	170-175	178-179[21]
2			4b	30	94	190-192	193-195[21]
3			4c	45	80	172	170[21]
4			4d	20	95	133-135	131-133[21]
5			4e	55	85	174-176	177-179[23]
6			4f	45	85	183	182-184[22]
7			4g	45	83	176	177-179[22]
8			4h	40	82	134-135	134-136[22]
9			4i	60	80	138-140	139-141[23]
10			4j	35	88	183-185	184-185[24]
11			4k	25	88	190-194	194-196[24]
12			4l	45	85	242-246	241-242[24]

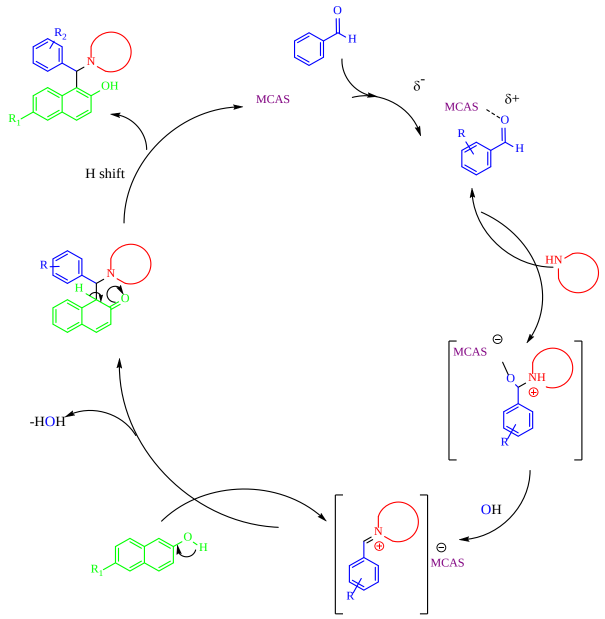
Then, different solvents and varies temperature were investigated. It was found that solvent-free conditions and room temperature were yielded the best results (**Table 2**, entry 5).

After optimizing the reaction conditions, to investigate scope and limitation of the present approach, various 1-(α-aminoalkyl) naphthol derivatives were synthesized.

The results showed in the synthesis of 1-(α-aminoalkyl) naphthols Fe3O4/cellulose/vitamin C composite as a solid catalyst was more effective, in comparison to fore-mentioned catalysts, giving excellent yields and requiring a shorter reaction time. A series of aldehyde and amines with 2-naphthol were reacted using Fe_3O_4/cellulose/vitamin C composite as a catalyst without solvent and the results were shown in **Table 3**. The reaction of the all aromatic aldehydes was performed almost equally well to obtain Betti base (4a–l) in excellent yields.

This protocol has the potency to sustain aromatic aldehydes with different substituents on the aromatic ring such as methyl, methoxy, nitro and halo groups. All of reactions had good yields. Surprisingly, the reaction was successful with aromatic amines. The Significant features of this method included operational simplicity, inexpensive reagents, no need for any additive to promote the reaction, high yields of products, short reaction times and the use of relatively nontoxic reagents and solvents, plus easy separation of heterogeneous catalyst by solubility in water and filtration .

A tentative mechanism for the reaction is proposed in Scheme.3. We assume that the Lewis acid–base interaction between the catalyst and the oxygen of the aldehyde carbonyl group leads to an electrophilic carbon atom. Condensation of the amine with activated aldehyde followed by dehydration generates an imine intermediate. Consequently, the nucleophilic attack of the 2-naphthol to imine gives the desired product as depicted in **Scheme 2**.



Scheme 2. assumed mechanism for the synthesis 1-(α-aminoalkyl) naphthol

RECYCLABILITY STUDY ON FE3O4/CELLULOSE/VITAMIN C COMPOSITE

One of the advantages of heterogeneous catalysts is their easy separation from the reaction mixture and ability for reusing in the system. In addition, the separation of the nano composite catalysts by external magnetit from the reaction mixture is much easier than other heterogeneous catalysts. In this regard, recyclability and reuse of Fe3O4/cellulose/vitamin C were evaluated in models reaction. Fe3O4/cellulose/vitamin C was recycled and used in model reaction at least for five times without any significant decrease in efficiency.

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