Novel biohybrid aerogel composites based on cellulosic and cobalt metallic nanoparticles: efficient and recyclable catalysts for green reduction reactions

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Abstract. In this study, a cellulose nanomaterial (Cellulose nanofiber, CNF) was employed as solid support and stabilizing agent for the highly active cobalt nanoparticles via an in situ green and facile synthesis as an environmentally benign supported catalyst. The process of preparation involves the reduction of cobalt precursors on the surface of CNF in ambient conditions with the presence of NaBH4. The structure of the synthesized organic-inorganic hybrid Co/CNF was characterized by field emission scanning electron microscopy, energy dispersive spectroscopy and Fourier transform infrared spectroscopy. The hybrid aerogel nanocomposite Co/CNF demonstrated excellent catalytic activity for the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) in water with NaBH4. Even with a very low amount of catalyst and was found to be good enough to achieve 100% reduction of 4-NP with a higher reaction rate (in 8 min). The heterogeneous nanocomposite catalyst was easily isolated from the reaction mixture by simple filtration and reused 5 times without significant loss of its catalytic activity.

1. Introduction
There is a growing need for environmentally benign, economic and highly active catalysts. Supported catalyst can play an important role in chemical reactions and environmental remediation. In recent years, investigations on supported heterogeneous catalysts become one of the major focuses of modern worldwide research in catalysis. This research has been directed towards the exploration of sustainable and ecological resources, in other words green chemistry.

Cellulose as the most abundant biopolymers in the world has attracted considerable attention as biomaterial support for catalytic systems due to their unique properties, their renewability, biocompatibility, biodegradability, non-toxicity, low-cost and environmental benefits. [1-3]

On the other hand, minimizing the size of solid heterogeneous catalysts to the nano-scale increases the specific surface area and the availability of active sites which improves the catalytic performances. The development of nano-sized systems as supported heterogeneous catalysts makes it possible to improve the reactivity and the selectivity of the catalysts compared to the non-supported and “homogeneous” ones [4].

Metal and metal oxide nanoparticles have attracted tremendous interest in catalytic applications in many important industrial processes, like those for the production of fine chemicals and pharmaceuticals.
[5] because of their versatile catalytic activities and high surface areas [6–9]. However, metal nanoparticles tend to agglomerate because of their high surface energy which reduces their catalytic performances. Moreover, there are no practical ways to recover the metal nanoparticles from the reaction medium, which presents an additional challenge that limits the usage of metal nanoparticles materials in catalysis. The effective approach to overcome these problems is immobilization of metal nanoparticles on different materials [10].

In this work, we developed a novel bio-hybrid aerogel based on cellulosic nanofibers and cobalt Metallic particles (Co/CNF) and investigated the catalytic performances of this nanocomposite material for the green reduction reaction of nitrophenol.

2. Material and Methods

2.1. Chemicals
Details about the materials and chemicals used for the TEMPO-catalyzed extraction of CNF can be found in a previously published work [10]. Cobalt (II) sulphate heptahydrate [CoSO$_4$.7H$_2$O], Sodium borohydride NaBH$_4$, 4-Nitrophenol (4-NP) and all solvents were obtained from Sigma-Aldrich and used as supplied without any purification.

2.2. Characterization techniques
FTIR spectra were recorded by BRUKER-Vertex 70. SEM was measured with TESCAN – VEGA3. EDX measurement was performed using AMETEK, EDAX- OCTANE PLUS. UV-Visible used for the kinetic study is a Shimadzu UV–vis spectrometer (UV-2450).

2.3. Preparation of the CNF
The rachis of date palm tree was used in this work as the original source of cellulose. Cellulose Nanofiber CNF was extracted following the procedure well described in our previous work [11].

2.4. Preparation of Co/CNF aerogels
Highly active cobalt nanoparticles supported by porous aerogels cellulose nanofiber composites (Co/CNF) were prepared by an environmentally benign method. The aerogel preparation begins with the formulation of a matrix based on cellulose nanofiber and CoSO$_4$. These two components were mixed by magnetic agitation and 5 minutes sonication to better homogenize the dispersion. After that, the composite mixture was treated with sodium tetrahydroboride NaBH$_4$ in distilled water and finally lyophilized as described in the Figure 1 below.

![Figure 1. Preparation of Co/CNF aerogels.](image-url)
2.5. **Catalytic Reduction of para-nitrophenol**

First, a solution of para-nitrophenol (4-NP) (0.5 g / l) is prepared, then 10 ml are taken from this solution and 10 equivalents of NaBH₄ with 5 mol% of Co/CNF are added with stirring magnetic at room temperature. The yellow color of the mixture decreases gradually and disappears after 8 minutes according to the following reaction (figure 2). The kinetic was followed using UV visible spectroscopy.

![Figure 2. Catalytic Reduction of para-nitrophenol.](image)

3. **Results and discussion**

3.1. **Aerogel Characterization**

The new recyclable and environmentally friendly hybrid aerogel composites catalysts Co/CNF was characterized by mean of FTIR spectroscopy, scanning electron microscopy (SEM) and elementary analysis (EDX). Figure 3 shows the SEM picture of pure CNF aerogel taken as reference and that of the Co/CNF aerogel composite. The SEM micrograph of cross section of the aerogel made of pure CNF (Figure 3-A) shows that the CNF are organized in films. The chemical groups carried by the CNF (OH and COOH due to the oxidation) allow H-bounding and permit the cellulose nanofibers to interact and form such a uniform structure [12]. Similar structure is observed for the aerogel composite Co/CNF (Figure 3-B). However, when zooming on the films (Figure 3-B), one can observe metal particles grafted on the films surfaces. At these magnifications, particles of about 1µm are detected but also few aggregates of more than 10 µm could be observed. But, in general, on can confirm that a good dispersion of cobalt particles is obtained. EDX analyses (Figure 3- C and D) confirm that these particles are composed of cobalt. At that level the type of interaction between the CNF film and the metal particle is of high importance. SEM analyses cannot give information about this inquiry. However, in our approach the cobalt particles are fixed by the hydrogen bonds to the CNF surface. It seems that the carboxylate groups at the CNF surface play an emulsifying effect to control the size and insure good dispersion of cobalt particles in the aerogel.
Figure 3. MEB and EDX characterizations of the CNF and Co/CNF composite aerogels.

Figure 4 present the FTIR spectra of the Co/CNF composite aerogel and that of the pure CNF aerogel taken as reference. Some characteristic bands related to the physical and chemical structure are the hydrogen-bonded OH stretching at ca. 4000–2995 cm$^{-1}$, the OH bending of adsorbed water at 1635 or 1638 cm$^{-1}$, the CH stretching at 2900 cm$^{-1}$, the HCH and OCH in-plane bending vibrations at 1430 cm$^{-1}$, the CH deformation vibration at 1375 cm$^{-1}$, the stretching vibration of C=O from the free COOH band near 1737 cm$^{-1}$, the C–OH out-of-plane bending mode at 668 cm$^{-1}$. Bands at 4000–2995 cm$^{-1}$, 2900 cm$^{-1}$, 1430 cm$^{-1}$, 1375 cm$^{-1}$, and 900 cm$^{-1}$ are especially sensitive to the state of the crystalline and amorphous regions. While comparing the two spectra, one can observe that the stretching vibration of C=O from the free COOH band near 1737 cm$^{-1}$ disappears from the FTIR spectrum of the composite. On the other hand the intensity of the band of C–OH out-of-plane bending mode at 668 cm$^{-1}$ strongly increases. These two observations might confirm that the COOH and OH groups of cellulose are involved in strong interactions with cobalt particles, which helped to ensure their stabilization and their good dispersion in cellulose matrix.

Figure 4. FTIR spectra of CNF and Cobalt/CNF composite aerogels.
3.2. Catalytic Activity
Initially, blank reactions without any catalyst were carried out; the results are shown in Figure 5. The p-NP demonstrated an intense UV absorption band at about 315 nm. After adding NaBH₄, it was found that the absorption band was shifted towards 400 nm due to the formation of nitrophenolate ions.

The Co/CNF demonstrated excellent catalytic activity towards the reduction reaction of para-nitrophenol to para-aminophenol in water. To our delight, even a very low amount of catalyst was also found to be good enough to achieve 100% reduction of para-nitrophenol with a higher reaction rate (8 min). Results of kinetic study of para-nitrophenol reduction with (Co/CNF) catalyst are shown in Figure 6. The high reaction rate could be explained by the immobilization of nanoparticles on a cellulosic catalytic support which increases surface area and makes cobalt metal nanoparticles more available and more accessible to the reagents in the reaction medium, and therefore increases the catalytic performance of the catalyst.

3.3. Recyclability Study
Co/CNF catalyst can be easily separated from the reaction mixture and reused with 100% reduction efficiency for five cycles. This catalyst has very interesting catalytic potential applications in eco-friendly processing and in heterogeneous catalysis and reduction reactions according to green chemistry.

Another important advantage of heterogeneous catalysis is the ease of separation from the reaction medium by a simple filtration and its reuse for another reduction reactions. In our case, after filtering the mixture at the end of the reduction reaction and washing the catalyst several times with distilled water, the catalyst was recycled several times to highlight its recyclability. The results of this recyclability study are presented in Figure 7.

These experiments were performed to test the catalyst recyclability. The results of the recyclability tests show that the regenerated catalyst has a good catalytic activity with a total conversion of reagent even at the 5th reduction cycle.

The heterogeneous catalyst Co/CNF possesses a high catalytic activity in the reduction reaction of para-nitrophenol to para-aminophenol by NaBH₄, taken as a model reaction.
On the other hand, from these results (figure 7) we can see that this reaction is of order 1; so the reaction rate is dependent of the concentration of the reactive.

![Figure 7. Recyclability study of Co/CNF Catalyst.](image)

4. Conclusion
We successfully synthesized a recyclable heterogeneous catalyst Co/CNF based on cellulose nanofibers (CNF) used as an ecologically catalytic support.

The microstructure investigations showed that Co nanoparticles are homogeneously dispersed in the walls of the CNF based aerogel. This heterogeneous catalyst shows a high catalytic activity towards the reduction reaction of para-nitrophenol with a 100% yield and was easy to recover and recycle. Moreover, it showed excellent reusability for five successive cycles with 100% reduction efficiency.

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