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Synthesis of BaCO₃ particles tailored by carboxylated cellulose fibers

A Jada^{1,2,4}, S Ladhari^{1, 2} and K Jradi³

¹ Institut de Sciences Des Matériaux De Mulhouse (IS2M-UMR 7361 CNRS- UHA), Mulhouse-France

² Université de Strasbourg, Strasbourg, F-67081, France.

³ Centre for Research on Lignocellulosic Materials. University of Quebec at Trois Rivières, 3351, boulevard des forges. Trois –Rivières, QC, G9A 5H7

⁴ Author to whom any correspondence should be addressed

amane.jada@uha.fr

Abstract. The present work deals with the use of carboxylated cellulose fibers, thereafter called Cellulose Nano Fibers (CNF), as eco-friendly materials and sustainable resources for remediation and valuation, of metal ions present in contaminated water. Barium divalent cation (Ba²⁺) is among the most common heavy metal pollutants found in water such as arsenic, cadmium, chromium, copper, nickel, lead and mercury. Thus, CNFs containing carboxylate groups were first prepared by the oxidation of the cellulose fibers using the NaOCl-NaBr-TEMPO system, and thereafter, they were used as adsorbent for Ba²⁺ ions removal from BaCl₂ aqueous solutions. Such Ba²⁺ removal was evidenced by the decrease of both the CNF surface charge and the CNF absorbance, upon the addition of the metal divalent cation, BaCl₂ to the CNF aqueous dispersions. It is shown that the interaction occurring between the fiber carboxylic groups and the positively charged metal ions, Ba²⁺, occurs via electrostatic interactions and leads to the CNFs –Ba²⁺ complex formation. In the second part of this work, we investigated the effect of the CNFs on the crystallogensis of barium carbonate particles, BaCO₃. Thus, the CNFs aqueous solution was first added to barium chloride BaCl₂ solution, and the mixture was stirred for a period of time (complexation time), prior the addition of sodium carbonate (Na₂CO₃) solution. The precipitation of barium carbonate particles in the presence of CNFs occurred at ambient temperature, in a water-jacketed Pyrex glass vessel. Finally, the resulting Barium carbonate- CNFs composites were examined by various methods such as Scanning Electronic Microscopy (SEM), and X-ray Diffraction. From the SEM data, two BaCO₃ morphologies were observed, dendritic and bent or rods particles, respectively, in the absence and in the presence of the CNFs.

1. Introduction

Barium carbonate (BaCO₃) is a mineral used in various applications such as in the production of optical glass, ceramic, barite, pigment and as a precursor for magnetic ferrites and ferroelectric materials [1-6]. At Standard Ambient Pressure and Temperature (T=298.15 K (25 °C), Pressure, P= 1 bar), witherite is the stable form of BaCO₃ and has the aragonite structure with space group Pmcn.

Several methods have been used to prepare BaCO₃ particles. Hence, Li et al., [7] have used, water in oil microemulsion, as crystallization medium to prepare BaCO₃ nanobelts and nanorods. These authors found that the BaCO₃ synthesis was function of main three parameters which are the reactant concentration, the surfactant and the aging time.



Thongtem et al., [8] prepared Strontium carbonate (SrCO_3) and Barium carbonate (BaCO_3) nanoparticles by sonochemical method using strontium nitrate or barium nitrate and sodium carbonate as starting materials at 80°C , and for 1–5 h. *Xu and Xue* [9] used hydrothermal method to prepare uniform hexagonal pencil-like BaCO_3 whisker, by the chemical reaction of barium chloride and urea. In the present work, barium carbonate (BaCO_3) particles were prepared from the mixture of BaCl_2 and Na_2CO_3 on the carboxylated cellulose nanofiber as support. The aim of this study is to show how modified cellulose nanofiber (CNF), specifically CNF bearing carboxylate groups, can be used as biomaterials for remediation and valuation, of metal ions such as Barium cations, present in contaminated water, with an ultimate interest in developing Barium carbonate-CNFs composites for various applications

2. Material and methods

The barium chloride salt, BaCl_2 (Rectapur), was used as received without further purification. The cellulose nanofiber used as additive in the BaCO_3 precipitation medium were obtained by TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl radical)-mediated oxidation and successive mild disintegration in water of native wood celluloses, [10]. This procedure is known to introduce carboxylate moieties on the cellulose structure and to preserve the micrometric length of the cellulose nanofibers (including both the crystalline and amorphous domains). The resulting individual cellulose nanofibers (CNF) have 3–4 nm wide and 30 nm to few microns in length, i.e. the nanofibers have aspect ratios greater than 100.

2.1. Determination of the CNF carboxylate groups amount and assessment of Interaction between Ba^{2+} and CNF carboxylate groups

The Cellulose Nano Fibers (CNF), in their oxidized form, were titrated by cationic surfactant, cetyltrimethylammonium chloride, CTACl, and the resulting Streaming Induced Potential, SIP, was measured by Müteck titrator (particle charge detection, PCD, Müteck instrument), to determine the carboxylate group's content present in the CNF, following a similar method as described elsewhere [11]. The same SIP measurement method, was also used to evaluate the interaction occurring between the CNF carboxylate groups and the Ba^{2+} cations. Thus, the fiber aqueous dispersion was placed in the measuring cylindrical cell and then was titrated with standardized BaCl_2 aqueous solution.

In order to assess the electrostatic interaction occurring in aqueous solution between the fiber carboxylic groups and the positively charged metal ions (Barium (II) cations), the UV spectrophotometry method, in the wavelengths range $\lambda=220\text{-}280\text{ nm}$ was used to measure the absorbance of the cellulose nanofibers, CNF, aqueous dispersions in the absence and in the presence of increasing BaCl_2 salt amounts

2.2. Preparation of barium carbonate particle on the CNF support

Barium carbonate particles were prepared in the absence and in the presence of cellulose Nanofibers CNF in solutions super saturated with BaCl_2 and Na_2CO_3 , at 20°C .

3. Results and discussions

The impact of BaCl_2 amount on the CNF aqueous dispersion absorbance is important and will help us to highlight the interaction mechanism occurring between the fiber carboxylic groups and the positively charged Barium cations. Figure 1 shows the absorbance variation versus the wavelength, λ , in the range $\lambda=220\text{-}280\text{ nm}$, for CNF aqueous dispersions, in the absence and in the presence of various BaCl_2 amounts.

3.1. Absorbance measurements

As can be seen in Figure 1, in all cases, the increase of the absorbance when λ decreases from 280 to 220 nm is due to the contribution from the Rayleigh scattering which increases proportion to particle size and smaller light wavelengths. Further, the absorbance of the CNF aqueous dispersions decrease substantially as the BaCl_2 amount, expressed in moles, increases. Such decrease in the absorbance is due to the neutralization of the CNF carboxylate groups (COO^-) by the barium cations Ba^{2+} , leading hence

to less ordered CNF structure in the aqueous solution, and likely to the settling of the CNF-Ba complexes.

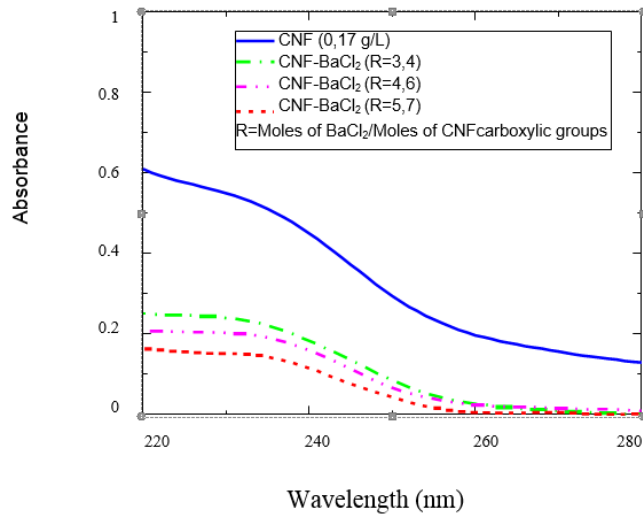


Figure 1. Absorbance of CNF aqueous dispersions, in the absence and in the presence of various BaCl₂ amount.

3.2. Streaming induced Potential

Figure 2 presents the variation of Streaming Induced Potential (SIP) of CNFs versus the amount of added divalent BaCl₂ salt, at constant initial salt concentration = 0.1 M. The curve in Fig. 2, shows that an increase in BaCl₂ amount leads to a decrease in the magnitude of the CNFs initial SIP value, and a plateau SIP value is reached at higher salt concentration.

As can be observed in the figure, diluted solution of Ba²⁺ divalent cations, exhibits an important decrease in the magnitude of the CNFs surface charge, without the solid surface charge sign reversal. Note that before any addition of BaCl₂ salt, the CNFs are initially negatively charged owing to the ionization of the carboxylate groups present on their surfaces. Thus, the addition of Barium ions leads to the formation of complexes between the Ba²⁺ cations and the CNF carboxylate groups reducing hence, the magnitudes of the CNFs surface charge and surface potential.

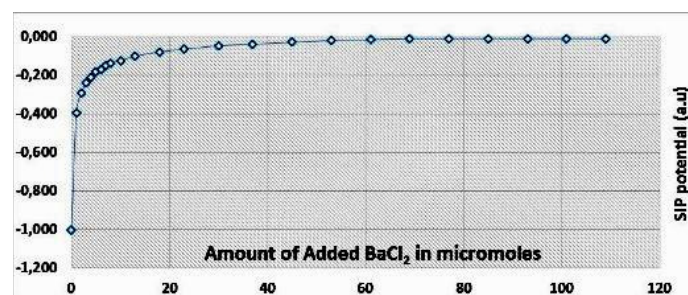


Figure 2. Titration of the CNF (1.74 mg) by BaCl₂ (0.1 M) aqueous solution.

3.3. Morphology and crystalline structure of barium carbonate particles as prepared in the presence of CNFs

Figure 3 presented the SEM micrographs of the CNF in the absence of BaCO₃ (Figure 3 a), the synthesized BaCO₃ in the absence of CNF (Figure 3b, dendritic structure), and the BaCO₃ (having belt and/or rod shapes) prepared on the CNF surface Figure 3c). The results obtained showed that CNFs form complexes with barium ions which modify their electrical charges, their textures and morphologies.

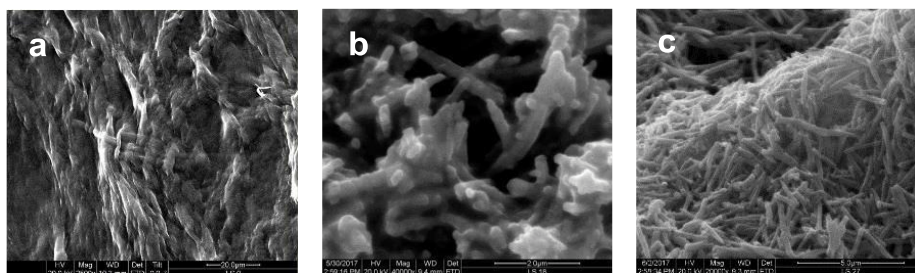


Figure 3. SEM images of (a) CNF; (b) BaCO₃ (dendritic structure) and (c) CNF- BaCO₃ (belt and/or rod structures) composite.

Furthermore, in the Barium carbonate-CNF composites, the barium carbonate (BaCO₃) particles are deposited on the surface of the CNF. The barium ions adsorbed on the surface of the cellulose fiber are transformed into barium carbonate particles with a rather narrow size distribution.

4. Conclusion

In this work, it was shown that Cellulose Nanofibers can be used as adsorbent for Ba²⁺ cations removal from water, and as support for the conversion of the CNFs –Ba²⁺ complexes, formed in situ, to metallic carbonate, BaCO₃ particles, anchored on the CNF surface. The final BaCO₃-CNF composite obtained is less toxic than Ba²⁺, and it has many chemical and industrial applications.

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