

Removal of calcium ions from water and its conversion to metal carbonate-cellulose nanofibers composites, by adsorption-complexation-precipitation method

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Abstract

Since the future of the science and the technology is gradually shifting towards the use of eco-friendly materials and sustainable resources and processes, researchers are very interested in using biomaterials for remediation and valuation, of metal ions in metallic polluted water.

In the present work, we have prepared cellulose nanofibers, CNFs, containing carboxylate groups by oxidation of the cellulose fibers using the NaOCl-NaBr-TEMPO system, thereafter, these CNFs were used as adsorbent for calcium ions removal from CaCl₂ aqueous solution. The calcium ions were eliminated from the solution due to electrostatic interaction occurring between the CNFs carboxylate groups and the calcium ions leading to CNFs –Ca²⁺ complex formation. Increasing the amount of carboxylate groups on the CNFs surface leads to enhanced removal amount of calcium ions from the solution. The calcium ion removal efficiency was further enhanced by the crystallisation of calcium carbonate, CaCO₃ particles on the CNFs surface, upon the addition of sodium carbonate (Na₂CO₃) aqueous solution to the CNFs – Ca²⁺ complex. The precipitation of CaCO₃ particles in the presence of CNFs occurred at ambient temperature, in a water-jacketed Pyrex glass vessel, and yielded CaCO₃-CNF composites in which the amount of nanofibers varied from 3 wt% to 28 wt%. The CaCO₃-CNF samples were then characterized by various methods such as Fourier Transform Infra Red (FTIR) microscopy, X-Ray Diffraction (XRD), Scanning Electronic Microscopy (SEM), and microelectrophoresis.

The SEM images showed that the CaCO₃ particles coated the cellulose nanofibers surface. The X-Ray analysis indicated the existence of two CaCO₃ polymorphs: calcite and vaterite. The X-Ray data showed that the CaCO₃ vaterite fraction is function of fiber amount in the CaCO₃-CNF composites. Furthermore, the CaCO₃ zeta potential was also dependent on the CNF amount. Hence, the increase of either the cellulose nanofibers amount or the cellulose nanofiber carboxylate content, in the CaCO₃ precipitation medium, lead to an increase of the CaCO₃-CNF composite zeta potential value. Finally, the presence of the CNF in the CaCO₃ precipitation medium was found to modify the texture and the surface morphology of the CaCO₃-CNF composite.

Keywords: Calcium carbonate, cellulose nanofibers, complexation, composite, wastewater remediation.

1. Introduction

Compounds such as ground (GCC) and precipitated calcium carbonate (PCC), kaolin, calcinated kaolin, titanium dioxide, talc, aluminum dioxide, are the most used fillers in pulp and paper manufacturing and coating, [1, 2]. Rougher and larger particles are used in fillers compared to the ones that are used in paper coating. Filler use has increased during the last decades as resulting from their special properties that bring to paper products. In the papermaking the amounts of fillers vary from none to at least 30% of the whole furnish. Fillers such as calcium carbonate (CaCO_3) particles play important roles in practically all printing and writing papers. The filler properties such as the particle size and the shape are important in determining the paper and paperboard properties, [3, 4]. In addition, CaCO_3 filler is used in printing and writing papers mainly to reduce the raw material costs and the basis weight of paper. However, the progressive addition of CaCO_3 in paper is limited by its negative effects on the bond strength and bending stiffness of paper, [5]. Increasing the amount of CaCO_3 filler in the paper have been investigated by several authors, [6-8]. Composite fillers, formed by the in-situ precipitation of CaCO_3 in a suspension of cellulosic fibers, have been shown to improve the performance of CaCO_3 and to allow increased amounts of filler in paper, [9, 10]. However, the mechanism by which the cellulosic fibers affect the CaCO_3 particle size and the crystal habit in the CaCO_3 -CN composites have not been examined in detail in these studies. The purpose of the present work is to use cellulosic nanofibers (CN) to investigate their effects on the CaCO_3 particle size, morphology, crystalline structure and electrical surface charges. Thus, CaCO_3 -CN composites were produced by precipitating CaCO_3 particles in the presence of three cellulosic nanofibers having various amounts of carboxylate groups. The mechanisms by which the cellulose nanofibers affect the CaCO_3 crystallogenes are highlighted.

2. Experimental procedures

2.1 Materials

The calcium and carbonate salts used as starting materials for the precipitation of calcium carbonate are, respectively, the calcium nitrate tetra hydrate $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ purchased from Prolabo and the sodium carbonate anhydrous (Na_2CO_3) purchased from Fluka Chemie AG. All reagents were used as received.

Three cellulose nanofibers used as additives in the CaCO_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, [11]. 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 have 3–4 nm wide and 30 nm to few microns in length, i.e. the nanofibers have aspect ratios greater than 100.

2.2 Preparation of CaCO_3 -CN composite particles

Supersaturated solutions for crystal growth experiments were prepared, at temperatures ranging from 20°C to 60°C, by addition of equal volumes of sodium carbonate (Na_2CO_3) to calcium nitrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) solutions in a water-jacketed Pyrex glass vessel of 300-mL capacity, as described elsewhere Jada, and Verraes (2003). In each experiment the final concentration of calcium solution, was kept equal to the final concentration of carbonate. In addition, the nano cellulose fiber aqueous solutions of NF1 or NF2 or NF4, were first added to calcium nitrate solution and the mixtures were stirred for about 30 min (complexation time) prior the addition of Na_2CO_3 solutions. The final cellulose fiber concentration in the precipitation medium, C_{fiber} , varied from 0.025 to 0.241 g. L⁻¹, while the final calcium concentration was kept constant and equal to 6.25 10⁻³ M. The final pH in the precipitation medium was around 10.3 ± 0.1. At the end of the CaCO_3 precipitation, the CaCO_3 -CN composite particles were recovered either by decantation or by filtration using 0.22 micrometre, GS Millipore filter type, and washed thoroughly with water to remove any fiber that is not involved in the composite. The washed composites were then dried under vacuum to thoroughly remove any traces of water.

2.3 Characterization methods of CaCO₃-CN composite particles

2.3.1 Streaming Induced potential measurement

Determination of the amount of the nano fibers carboxylate groups

The nano fiber carboxylate groups' amount was evaluated by titration of the fiber aqueous dispersion with a cationic surfactant (cetyltrimethylammonium chloride, CTACL) and using a potential measuring device (particle charge detection, PCD, Müteck instrument). The measuring cell is composed of a cylindrical poly (tetrafluoroethylene) (PTFE) container with a PTFE piston inside. The titratable aqueous fiber dispersion (10 ml) was filled into the gap (0.5 mm) between the container wall and the piston, and various amounts of the aqueous cationic surfactant solution were then added. The resulting streaming induced potential (SIP) was measured between two gold electrodes located at the top and the bottom of the gap. During the measurements the piston moves sinusoidally up and down at a frequency of 4 Hz and forces the aqueous suspension to move and to stream through the gap along the container wall. The SIP measured during the piston movement, results from the distortion of the diffuse double layer of the fiber particles adsorbed on the container wall. It should be mentioned that the PCD Müteck instrument allows the measurement of only relative potential values, [12].

2.3.2 Fourier Transform Infra Red spectroscopy

Infrared spectra (IR) of the CaCO₃-CN composites were recorded on a Bruker IFS 66 IR spectrometer with, 7 mm aperture setting, Drift sample form, MCT detector, KBr beam splitter, 4000 cm⁻¹ start frequency limit for file, 600 cm⁻¹ end frequency limit for file, and analysed with OPUS software. The number of scans was fixed at 100 with a resolution of 4 cm⁻¹.

2.3.3 XRD analysis

The polymorphs of CaCO₃-CN composites were identified at ambient temperature by powder X-ray diffraction (PHILIPS diffractometer), with Cu anticathode at 40 kV Voltage and 30 mA current. XRD patterns of the samples were collected from 20 to 60 degrees scanning angle, and at wavelength $\lambda_{K\alpha 1}=1.54056 \text{ \AA}$.

2.3.4 Scanning Electronic Microscopy (SEM) analysis

The CaCO₃-CN composite particles were gold coated in vacuum and then examined by scanning electron microscope (Environmental Scanning Electron Microscope FEI Model Quanta 400). The SEM analysis was performed by using an accelerating voltage of 20 kV, a horizontal configuration, Tilt=0° and magnifications ranging from 500x to 16000x.

2.3.5 Electrophoretic mobility measurement

Determination of CaCO₃ surface charges

The measurements of the electrophoretic mobility (U_e) of the CaCO₃-CN composite particles were performed in a clean electrophoresis chamber, filled with the composite aqueous dispersion and submitted to an electrical field for a few seconds. The tension applied in the electrophoretic cell was 100 V. At least three experiments were achieved for each sample. The mobility U_e is calculated according to eq (1):

$$U_e (\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}) = 10^{-4} v (\mu\text{m s}^{-1})/E (\text{V cm}^{-1}) \quad (1)$$

where $v (\mu\text{m s}^{-1})$ is the velocity of the CaCO₃-CN composite particles measured at ambient temperature by using the Zetaphoremeter II apparatus [13], and $E (\text{V cm}^{-1})$ is the electric field applied to the CaCO₃-CN composite aqueous dispersion.

3. Results and discussion

3.1. Amount of the cellulose nanofibers carboxylate groups

The cellulose nano fibers (CN) used as additives in the crystallogenesis of the CaCO₃ particles are presented in [Table 1](#). As can be seen in this table, the fibers are oxidized and contain various amounts of carboxylate groups. It should be noted that the carboxylate content of each cellulose nanofibers was determined using an electrical conductivity titration method as described elsewhere, [11].

[Table 1](#)

In addition, the anionic cellulose nanofibers aqueous solutions were titrated with the cationic CTACL and the SIP (see paragraph 2.3.1) was measured after the addition of various amounts of the aqueous cationic surfactant solution. The variations of the normalized SIP for the various cellulose nanofibers, as function of CTACL surfactant concentration, expressed as the ratio R of the final CTACL concentration to cellulose nanofibers concentration, are shown, in [Fig 1](#).

[Fig. 1](#)

As can be seen in [Fig 1](#), all the cellulose nanofibers are negatively charged as resulting from the ionization of the COONa surface groups of the fiber. Upon the addition of the cationic CTACL molecules, the negative surface charges of the cellulose nanofibers are neutralized and charge reversal occurs at high CTACL concentration. The CTACL concentration at which the SIP value of the cellulose nanofiber is zero corresponds to the Point of Zero Charge (PZC) of the cellulose nanofibers. The PZC values of various cellulose nanofibers are gathered in [Table 1](#), and are expressed as the ratio R of the final CTACL concentration to cellulose nanofiber concentration. Further, [Fig 1](#) indicates in all instances, that as the CTACL concentration increases, the amplitude of the SIP decreases up to the PZC above which charge reversal occurs, and then increases and reaches a plateau value. The data indicate that depending on the cellulose nanofiber type different PZC values may be obtained. Accordingly, it is expected that the NF4 as compared to NF2 fiber will interact more efficiently with calcium ions during the CaCO₃ precipitation experiments.

Finally, as shown in [Fig 2](#), a correlation is found between the cellulose nanofiber equivalent charge and cellulose nanofiber carboxylate amount of the various cellulosic fibers investigated in the present work.

[Fig. 2](#)

3.2. Crystalline structures of the CaCO₃ in the CaCO₃-CN composite as determined by FTIR spectroscopy

[Fig 3](#) presents the FTIR spectrum of the composite CaCO₃-CN prepared in the presence of the NF4 at temperature T=20°C and fiber concentration, C_{fiber} = 0.12 g. L⁻¹. As can be seen in [Fig 3](#), the various peaks (713 cm⁻¹, 745 cm⁻¹, and 875 cm⁻¹) were assigned to various CaCO₃ polymorphs, and the CaCO₃ vaterite fraction in the CaCO₃-CN composite was then calculated from the peak areas ratio of 745 cm⁻¹ to 876 cm⁻¹.

[Fig. 3](#)

In addition, an increase of the vaterite fraction in the CaCO₃-CN composite when the fiber concentration, C_{fiber} increases in the range 0.02-0.12 g.L⁻¹, was observed, as shown in [Fig 4](#), for the NF4 fiber at CaCO₃ precipitation temperature T=20°C.

[Fig. 4](#)

3.3. Crystalline structures of the CaCO₃ in the CaCO₃-CN composite as determined by XRD analysis

[Fig 5](#) shows the X-Ray spectrum of CaCO₃-CN (NF4) composite as prepared at T=20°C by precipitating the CaCO₃ particles in the presence of cellulose nanofiber NF4 type. As can be seen in [Fig 5](#), the main crystalline structure of CaCO₃

particles in the CaCO₃-CN (NF4) composite is calcite. In the almost samples of CaCO₃-CN prepared in the presence of the cellulose fibers NF1, NF2 and NF4 and analyzed by XRD, the CaCO₃ particles crystalline structures were mainly calcite with vaterite fractions that do not exceed 10 %.

Fig. 5

3.4. Morphological characteristics of the CaCO₃-CN composites as determined by SEM analysis

The morphological characteristics of CaCO₃ particles precipitated in the presence cellulose nanofibers (CN) were investigated by SEM. The SEM micrographs of the CaCO₃ particles prepared in the absence of cellulose nanofiber, and the CaCO₃-CN composites prepared in the presence of NF1 and NF4 cellulose fibers are shown, respectively, in Figs. 6 and 7A, 7B.

Fig. 6

Fig. 7A

Fig. 7B

As can be observed in Fig 6, heterogeneous CaCO₃ particles having rhombohedral and spherical morphologies, sizes ranging from 6 to 9 microns, and crystalline structure consisting of mixture of calcite and vaterite, are obtained in the absence of the cellulose fibers. However, in the presence of NF1 or NF4 cellulose nanofibers, the SEM micrographs shown in Figs 7A and 7B indicate homogeneous CaCO₃ particles having almost rhombohedral shape, mainly calcite crystalline structure, and mean particle size around 4-10 microns. It is apparent from SEM micrographs in Figs. 7A and 7B that the textures and surface morphology of the CaCO₃-CN composites are different from the SEM micrograph in Fig 6 of CaCO₃ particles, indicating the role of cellulose nanofibers in the modification of both the CaCO₃ crystallogenes and the CaCO₃-CN composite films properties. Moreover, SEM pictures (Figs 7A and 7B) of CaCO₃-CN composites reveal clearly the deposition of CaCO₃ particles on the surface of cellulose fibers. As shown in Fig 7B, CaCO₃ agglomerates are observed to be deposited and uniformly coating the cellulose fiber surface

3.5 Surface charge of the CaCO₃ particles in the CaCO₃-CN composite as determined by electrophoretic mobility

Fig 8 shows the zeta potential values of the various CaCO₃-cellulose fiber composites prepared in the presence of NF1, NF2 and NF4 cellulose nanofibers.

Fig. 8

For comparison the zeta potential value of the CaCO₃ particles prepared in the absence of the cellulose fiber is also shown in Fig 8. As can be seen in this figure, the overall samples give negative and low zeta potential values near the PZC value of the CaCO₃ particles. However, an increase in the magnitude of the zeta potential can be observed in Fig 8, when going from NF2 to NF4, i.e. when the cellulose nanofiber carboxylate amount increases. This finding indicates that the whole fiber surface in the CaCO₃-cellulose fiber composites is not totally covered by the CaCO₃ particles.

Conclusion

In this work, the textures, the morphologies, the particle sizes and the particle surface charges of the CaCO₃-CN composites were determined. The carboxylate content of the cellulose nanofiber was varied and was found to affect the

crystallogenesis of the CaCO₃ particles and the CaCO₃-CN composite characteristics. The resulting CaCO₃-CN composites were found to be harder than the powdery CaCO₃ sample. Further, homogenous textures of CaCO₃-CN composites having CaCO₃ rhombohedral shape were precipitated. Primary or agglomerated CaCO₃ particles were deposited on the cellulose nanofiber surface. Moreover, an increase in the vaterite fraction in the CaCO₃-CN composites was observed when either the fiber carboxylate content or the fiber concentration, in the CaCO₃ precipitation medium, increased. Such increase in the vaterite fraction resulted from the efficient complexation that occurs between calcium ions and the fiber carboxylate groups.

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References

- [1] Zhao, Y. L., Hu, Z. S. Ragauskas, A, Deng, Y. L.: [Improvement of paper properties using starch-modified precipitated calcium carbonate filler](#), Tappi Journal, 4, 3-7 (2005).
- [2] Han, Y. S., Hadiko, G., Fuji, M., Takahashi, M.: [Effect of flow rate and CO₂ content on the phase and morphology of CaCO₃ prepared by bubbling method](#). Journal of crystal growth. 276, 541-548 (2005).
- [3] Bown, R.: [A review of the influence of pigments on papermaking and coating](#), Transactions of the 11th Fundamental Research Symposium, Vol.1, Cambridge, Pira International Publications, UK, 83-137 (1997).
- [4] Fairchild, G. H.: [Increasing the filler content of PCC-filled alkaline papers](#). Tappi J. 75, 85-90 (1992).
- [5] Holik, H.: [Handbook of Paper and Board](#), published by Wiley- VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 33 (2006).
- [6] Middleton, S. R., and Scallan, A. M.: [The preparation of lumen-loaded pulp](#). Transactions of the 8th Fundamental Research Symposium, Oxford, Mechanical Engineering Publications Limited, London. Vol. 2, 613-630 (1985).
- [7] Allan, G. G., Carroll, J. P., Jimenez, G., and Negri, A. R.: [Enhancement of the optical properties of a bagasse newsprint furnish by fiber-wall-filler](#). Cellulose Chemical Technology. 32, 339-347 (1998).
- [8] Klunness, J. H., Caulfield, D. F., Sachs, I. B., Skyes, M. S., Tan, F., and Shilts, R. W.: [Method of fiber loading a chemical compound](#), US Patent 5, 223, 090 (1993).
- [9] Silenius, P.: [Improving the combinations of critical properties and process parameters of printing and writing paper and paperboards by new paper-filling methods](#). Doctoral thesis, Helsinki University of Technology, Laboratory of Paper Technology, Espoo, Finland, Report Series A14. 129p (2002).
- [10] Subramanian, R., Maloney, T., and Paulapuro, H.: [Calcium carbonate composite fillers](#), Tappi J. 4 (7), 23-27 (2005).
- [11] Saito, T., Nishiyama, Y., Putaux, J.L., Vignon, M., Isogai, A.: [Homogeneous Suspensions of Individualized Microfibrils from TEMPO-Catalyzed Oxidation of Native Cellulose](#). Biomacromolecules. 7, 1687-1691 (2006).
- [12] Wäsche, R., Steinborn, G.: [Characterization of the secondary properties of alumina, CFI \(Ceramic Forum International\)/Ber \(Bericht\)](#). (Deutsche Keramische Gesellschaft) DKG. 74 (5), 235-239 (1997).

[13] Jada, A., Verraes, A.: [Preparation and microelectrophoresis characterisation of calcium carbonate particles in the presence of anionic polyelectrolyte](#). *Colloids and Surfaces A physicochemical and engineering aspects*. 219, 7-15 (2003).

[Figures and Tables captions](#)

Fig. 1 Titration of various CN samples by aqueous solution of CTACL 0.1 M.

Fig. 2 Variation of the CN equivalent charge with the CN carboxylate amount

Fig. 3 FTIR spectrum of CaCO₃-CN (NF4) as prepared at 20°C

Fig. 4 Effect of the CN (NF4) concentration on the vaterite fraction in the CaCO₃-CN (NF4) composite prepared at T=20°C.

Fig. 5 X-Ray spectrum of CaCO₃-CN (NF4) as prepared at 20°C [Ca²⁺]=[CO₃²⁻]= 6.25 10⁻³ M, C_{fiber}=0.12 g. L⁻¹

Table1 Characteristics of the cellulose nanofibers (CN)

Fig. 6 CaCO₃ particles prepared at T=20°C, in the absence of CN [Ca²⁺]=[CO₃²⁻]= 6.25 10⁻³ M

Fig. 7A: CaCO₃ particles prepared at T=20°C, in the presence of CN (NF1), [Ca²⁺]=[CO₃²⁻]= 6.25 10⁻³ M

Fig. 7B: CaCO₃ particles prepared at T=20°C, in the presence of CN (NF4), [Ca²⁺]=[CO₃²⁻]= 6.25 10⁻³ M

Fig. 8: Zeta potential of CaCO₃ particles prepared at T=20°C, in the absence and in the presence of various CN: NF1, NF2 and NF4. [Ca²⁺]=[CO₃²⁻]= 6.25 10⁻³ M

Fig. 1

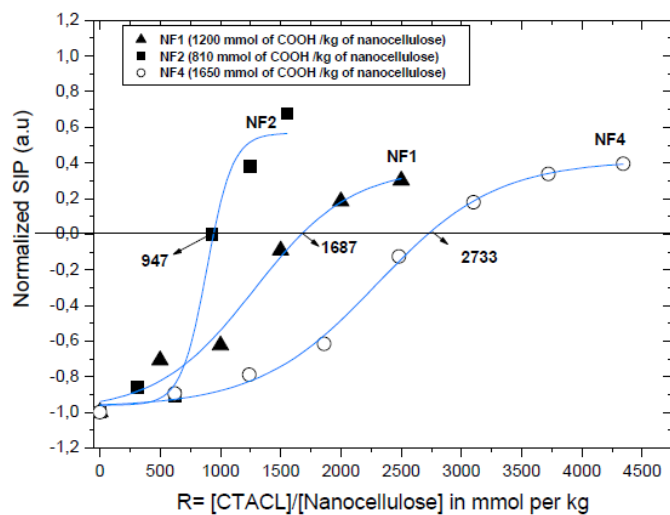


Fig. 2

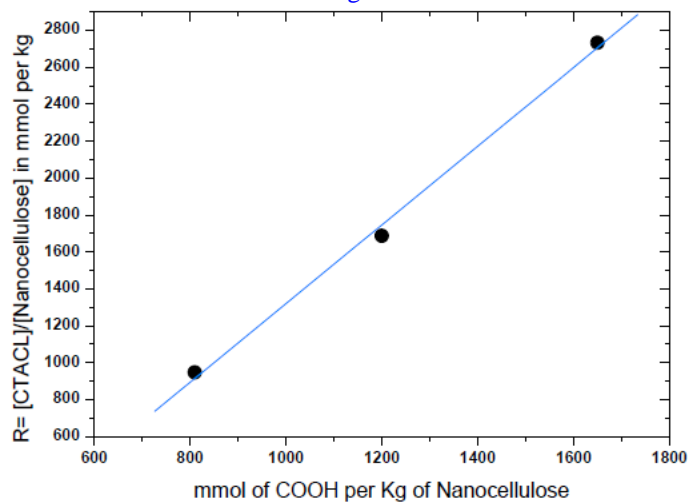


Fig. 3

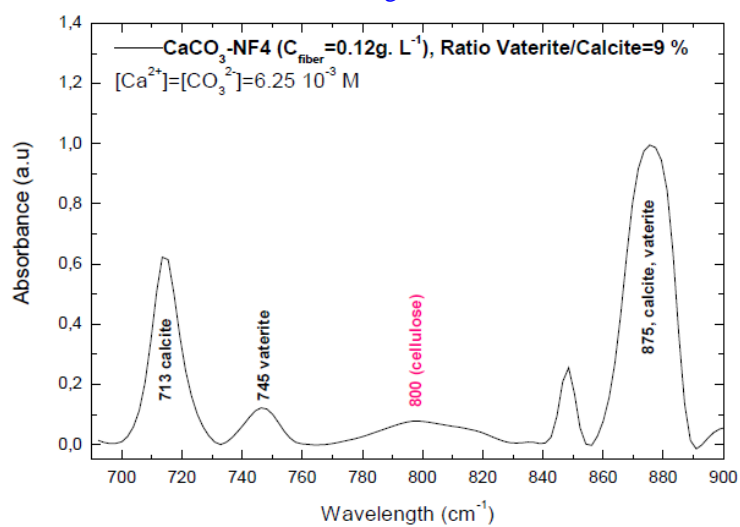


Fig.4

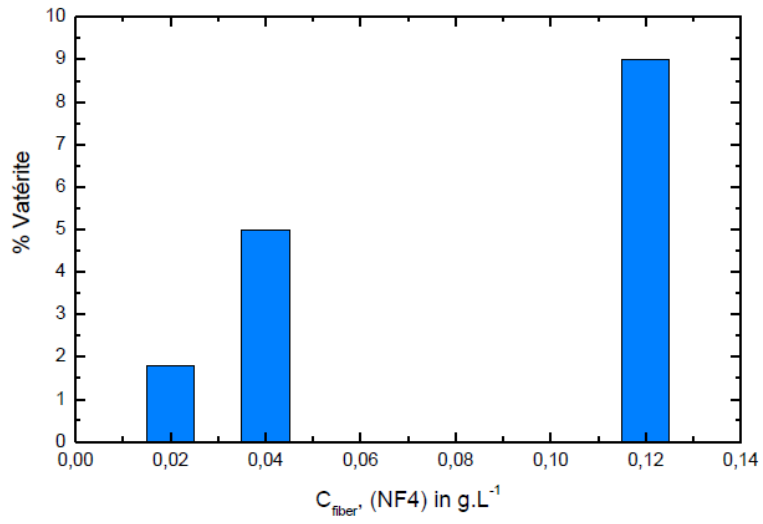


Fig. 5

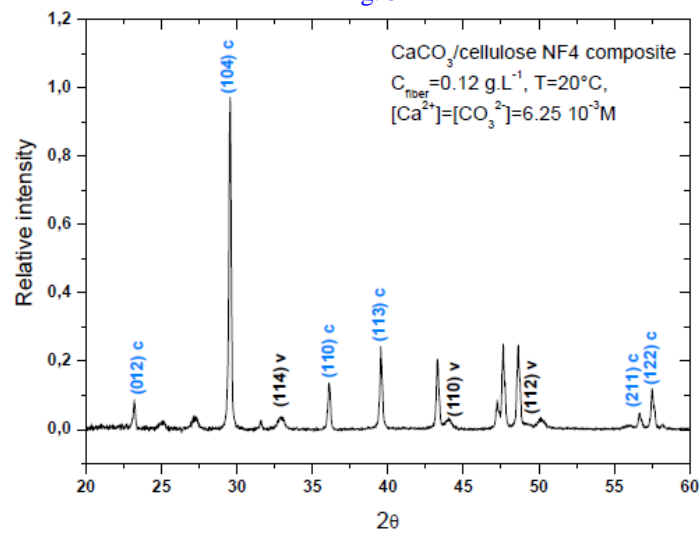
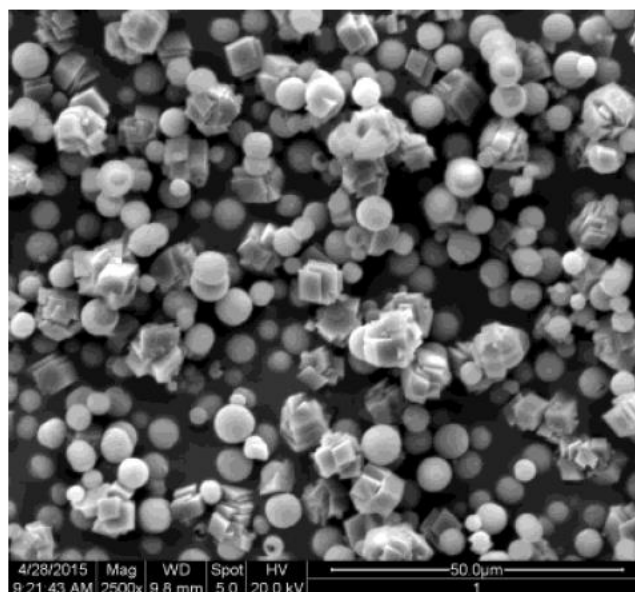


Fig. 6



Figs 7A and 7B

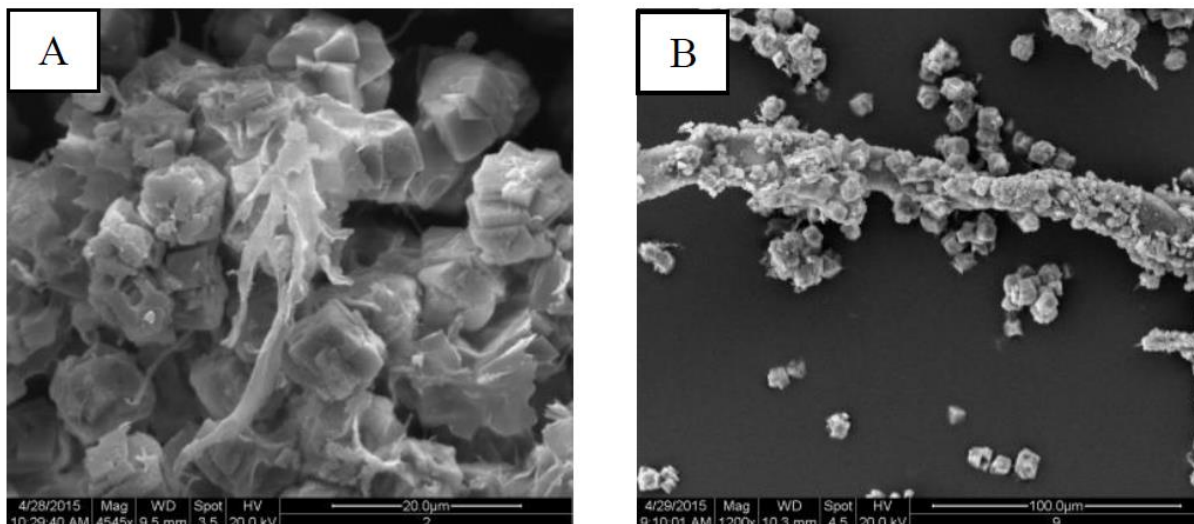


Fig 8

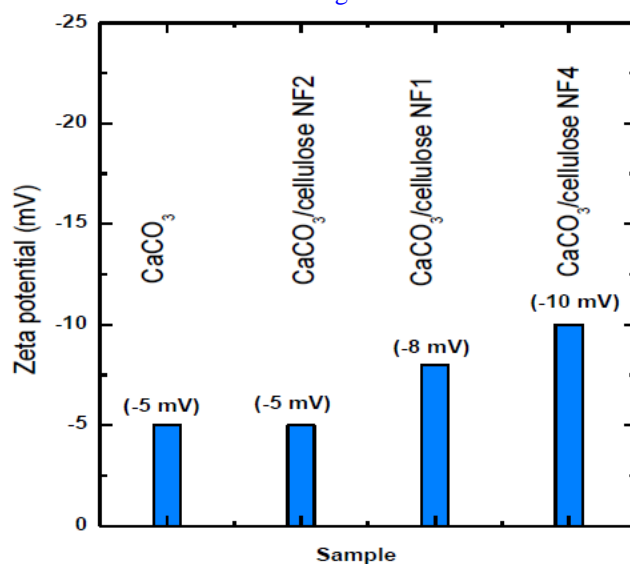


Table 1

CNF	Initial fiber concentration (g. L ⁻¹)	Amount of carboxylate groups (mmol per Kg of the nano fiber)
NF1	1.608	810
NF2	1.008	1200
NF4	0.806	1650
NF6	1.176	1749