O PAPEL vol. 82, N.º 11, pp. 84 - 89 - NOV 2021

DRYING ALTERNATIVES AND THEIR EFFECTS ON CELLULOSE NANOCRYSTAL REDISPERSION

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ABSTRACT

Cellulose nanocrystals (CNC) are the highly-ordered crystalline domains of lignocellulosic materials very abundant in nature, with high crystallinity, purity and mechanical and multifunctional properties favorable for various applications.

They are commonly isolated by acid hydrolysis in the form of stable aqueous suspensions in low concentrations. One of the critical points for obtaining an individualized and dried form is the drying step, due to the aggregation of the nanocrystals.

The consequence is that the recovering of rehydrated and isolated CNC is low. After dehydration of the material in considerably-high temperatures, the aggregation is promoted by hydrogen bonds between the surfaces of the CNC nanocrystals, promoting a loss of the nanometric dimension. Thus, in order to minimize CNC agglomeration, the effects of some conditions were studied: (a) whether or not to perform dialysis in CNC suspensions, and (b) addition of anti-binder agents (glycerin or dodecyltrimethylammonium bromide - DTAB). To study the drying alternatives, some of the CNC suspensions of 1% w/v extracted from cotton fibers were subjected to drying by evaporation in an oven with forced air circulation. Firstly, the pH of the stock suspensions, with and without dialysis, was adjusted to ~7. Each test was sonicated, and each anti-binder agent (0.8% w/v) was added separately to the suspension. The dried CNCs were redispersed, sonicated and centrifuged. More-satisfactory results were obtained from the dialyzed sample with a recovery efficiency of 35.2%. The same, without dialysis, was 15.6%. The addition of glycerin and DTAB showed a recovery efficiency of 30.6% and 49.6%, respectively. The dynamic light scattering technique was used to determine the average equivalent CNC diameter and zeta potential for all tests. The values found are within ranges equivalent to those normally found in literature (100-300 nm and -50 to -25 mv, respectively). None of the samples showed significant differences in morphology and dimension between the recovered CNC and the reference ones.

Keywords: *Cellulose nanocrystals, evaporative drying, glycerin, dodecyltrimethylammonium bromide, recovery efficiency.*

INTRODUCTION

Cellulose nanocrystals (CNC) are the highly-ordered crystalline domains of fibrous lignocellulosic materials isolated by chemical treatment, which make it possible to obtain well-defined nanoparticles (BRINCHI et al., 2013; LEE et al., 2019). In addition to being very abundant in nature and renewable, CNCs led to a significant improvement in mechanical and functional properties, satisfactorily acting as reinforcements in polymeric matrices (SILVA and D'ALMEIDA, 2009).Therefore, its dispersibility as individual particles and free of aggregates is essential for the efficiency of its applicability. In addition, commercialization in the dried form can facilitate its handling, storage, transport and durability (ESPARZA et al., 2019). However, the removal of water during the drying step can potentialize hydrogen bond development between cellulose nanocrystals which, although relatively weak, are difficult to break with the redispersion of the material in an aqueous medium, maintaining the aggregate form. Consequently, the morphology, surface charge and dimensions of these structures are different when compared to their characteristics before drying, compromising their integrity and properties as nanoparticles (TINGAUT, ZIMMERMANN and LOPEZ-SUEVOS, 2010; BECK et al., 2012).

Knowing that this modification of the nanocrystals surface can be done in a way that does not damage the cellulosic material structure, maintaining its morphological and dimensional characteristics during the drying process, this study aims to prevent/minimize the formation of hydrogen bonds, during cellulose nanocrystal drying, with the addition of chemical substances to the cellulose nanocrystals suspensions in order to improve the recovery efficiency of CNC after the drying step, improving its dispersion when applied to polymeric matrices. Both the cellulose nanocrystals that were dried by evaporation and those that were added the potential anti-binder agents were characterized, quantified and had their dimensions and surface charge compared with the respective reference tests.

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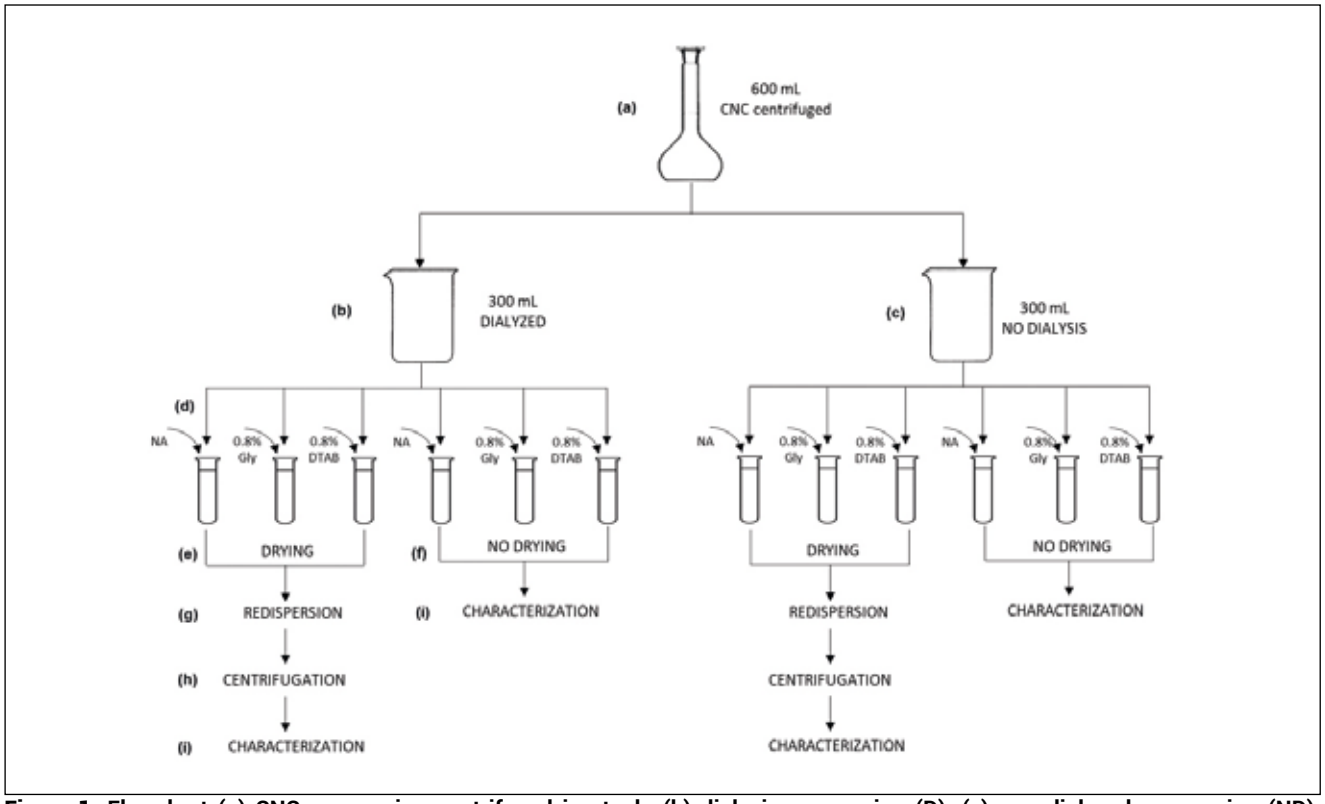

Figure 1. Flowchart (a) CNC suspension centrifuged in stock; (b) dialysis suspension (D); (c) non-dialyzed suspension (ND); (d) reference samples (NA), and addition of anti-binder agents (0.8%); (e) oven drying (DRY); (f) without drying (NODRY); (g) redispersion of dry CNC followed by sonication; (h) centrifugation to remove waste; (i) characterization by DLS and potential zeta. Anti-binder agents: glycerin and dodecyltrimethylammonium bromide

METHODS

The study was carried out using cellulose nanocrystal aqueous suspensions of 1% w/v, obtained from cotton fibers pretreated with 2% w/v NaOH. Hydrolysis was performed using sulfuric acid in the following condition (65% w/w acid; 50 min; 50°C and dry material acid ratio 20:1 v/w), according to Santana et al. (2019). To evaluate the effect of the dialysis step on CNC dispersion (D and ND, with and without dialysis, respectively) and the addition of anti-binder agents (GLY- glycerin and DTAB-cationic surfactant, 0.8% CNC, base dried) after drying (DRY and NODRY, with and without drying), the stock suspension (a) was divided into two equal parts to perform the tests (Figure 1).

Dialysis step and pH adjustment

The dialysis of some CNC suspensions was performed with a cellulose membrane (molecular weight cut off/MWCO 3,500) for sufficient time until the gradient between the distilled dialysis water pH and the suspension pH reached a value close to 4. Both the dialyzed suspension (pH 3.7) and the non-dialyzed suspension (pH 2.3) had their pH values adjusted to ~7, with 0.1 and 1 M NaOH solutions under constant agitation.

Preparation and addition of anti-binder agents

Possible anti-binder agents were used: (a) glycerin (GLY) P.A. 99.5% (Synth), as a wetting agent, and (b) dodecyltrimethylammonium bromide (DTAB) P.A.> 98% (Sigma), as a cationic surfactant. For each test, 100 mL of the CNC suspension was sonicated for 10 min (frequency 50/60Hz, RMS power 135 W), to enhance the nanocrystals dispersion. Then, under magnetic stirring, a dosage of 0.8% (w/v) of these chemical agents was added slowly and separately. Then, this volume was divided equally for the drying effect evaluation on the characteristics of the nanocrystals, generating two distinct 50 mL tests. For reference samples, the procedure was similar, however, without the anti-binder agent.

Drying of suspensions by evaporation

Drying of the samples was performed by evaporation in an oven with forced air circulation in glass containers at a temperature of 105°C, until the samples reached the gel point (approximately 20% w/v). Then, the material was dried completely, at 60°C. The dry CNC remained in the glass containers until redispersion.

Redispersion of the dried CNC

The dried CNC samples were rehydrated individually during 4 hours with distilled water, maintaining the same volume before drying, and sonicated for 60 min. Later, as there were still sedimented residue, the samples were centrifuged at 12,000 rpm (16,580 G), for 15 minutes, at

23°C. The supernatants were reserved for quantification and characterization. Samples that were not subjected to the drying step were also sonicated before characterization (DITZEL et al., 2017). All samples were stored in glass containers with a lid and placed under refrigeration (4ºC) until they were subjected to characterization.

Estimation of CNC recovery after the drying step

As the samples submitted to drying showed residue after redispersion, they were centrifuged as previously described, generating an acceptable supernatant (CNC suspension) and a sedimented residue (step rejection). To estimate the recovery, it was essential to know the dry dispersed solids content of the supernatants for each test. This determination was done by estimation using the turbidity of the sample. To obtain the calibration curve, the non-dried CNC samples were used with a known concentration of 1% (w/v). To obtain the curve's plotting data, the suspension was diluted to lower concentrations ones and had their turbidity equivalent measured, in NTU. Two curves were obtained, with and without dialysis, Figures 4 and 5, respectively.

Suspensions characterization

The Dynamic Light Scattering (DLS) technique was used to determine the average particle size (nm) considering its Brownian motion, and the zeta potential measurement (Zetasizer, Nano Series by Malvern Instruments), to evaluate the colloidal dispersion stability through the surface charge (mv). Initially, the samples were sonicated for 20 minutes to ensure the dispersion of the samples' nanocrystals before and after the drying step. Three independent measurements were obtained for each sample, at room temperature (25ºC), with a fixed detection angle of 173° and a laser beam wavelength of 633 nm. The size distribution was obtained by the Laplace inversion of the scattered intensity correlation function by the NNLS method. Each result represents the average value of the size distribution of the various particles dispersed in an aqueous medium.

RESULTS AND DISCUSSION

Characterization of the initial samples

It can also be observed that the sample-size distribution profiles with dialysis (Figure 2, A) and without dialysis (Figure 2, B) were uniform with equivalent mean diameter values of 113.2 ± 0.6 nm and 124.0 ± 0.2 nm, respectively. These results are in accordance with literature for cotton fiber CNC, 100-300 nm (SOUZA LIMA and BORSALI, 2004) and 161.3-175.6 nm (SANTANA et al., 2019). For the surface charge, the distribution profiles of the initial CNC stock suspensions, with dialysis (Figure 3, A) and without dialysis (Figure 3, B), were also uniform with mean values of potential zeta of -40.0 ± 0.4 mV and -45.2 ± 1.2 mV, respectively. All the samples can be considered as stable since the zeta potential has a modulus greater than 25 mV (MIRHOSSEINI; TAN; HAMID; YUSOF; 2008).

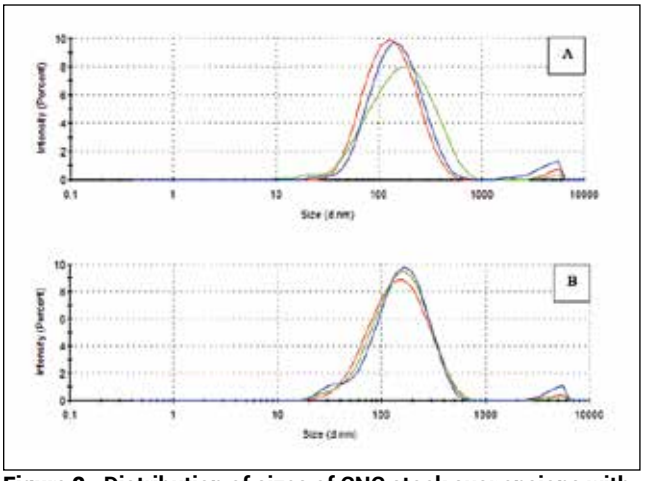

Figure 2. Distribution of sizes of CNC stock suspensions with dialysis (A) and without dialysis (B) as a function of intensity

Peng, Gardner and Han (2012) examined the effect of different drying alternatives for cellulose nanocrystals (CNC) and cellulose nanofibrils (CNF), including the oven-drying method. The results of dynamic light scattering of the redispersed CNC samples showed average diameter values of 91–295 nm, and morphology with smoother surfaces than those of the NFC, indicating denser packaging for CNC. However, the creation of highly agglomerated structures with multiscale dimensions was observed. The authors concluded that, in terms of the production of nanomaterials from cellulose suspensions, spray drying has greater potential for obtaining particles at nanoscale. This technique is not part of the scope of this study.

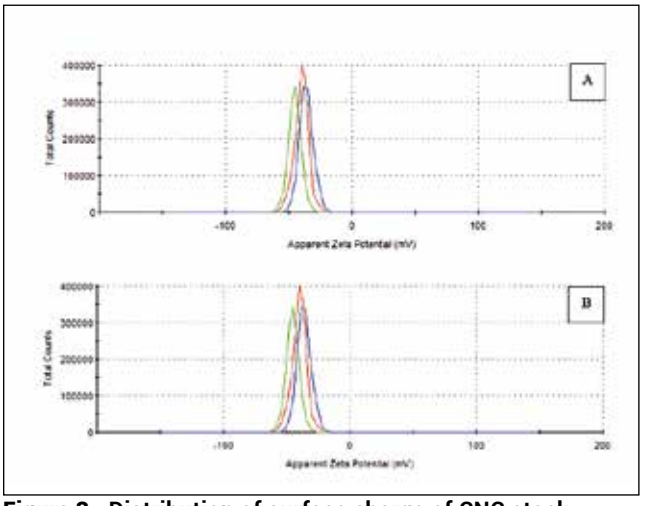

Figure 3. Distribution of surface charge of CNC stock suspensions with dialysis (A) and without dialysis (B)

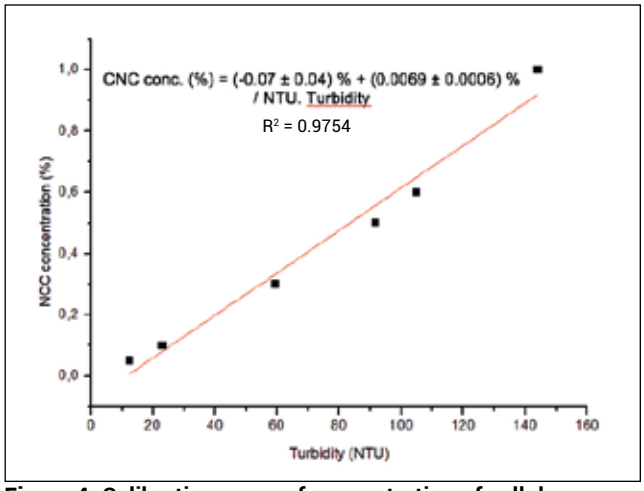

Figure 4. Calibration curve of concentration of cellulose nanocrystals as a function of turbidity for the dialyzed sample without drying

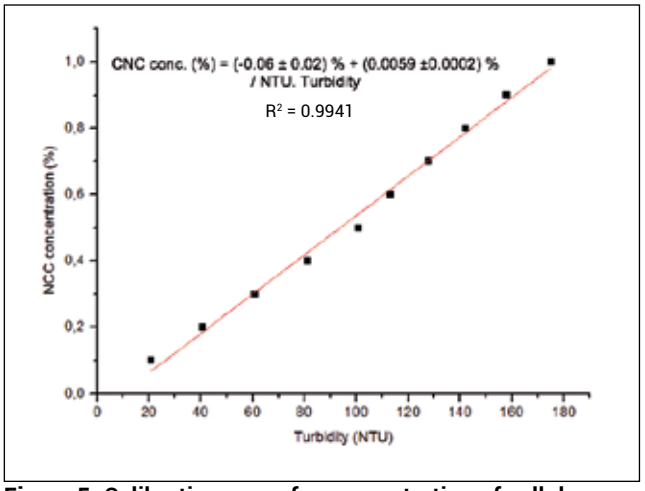

Figure 5. Calibration curve for concentration of cellulose nanocrystals as a function of turbidity for the non-dialyzed non-dried sample

Estimated CNCs recovery after drying

The calibration curves and correlation between the concentration of the CNC suspension (y) and turbidity (x) were constructed for CNC suspensions with dialysis and without drying (Figure 4) and suspensions without dialysis and without drying (Figure 5). Then, the supernatants from the centrifugation stage, after redispersion of the dried CNC, had their turbidity measured and concentrations estimated through the correlations found. With this concentration estimated in the supernatants, it was possible to estimate the CNC concentration that was recovered in the supernatant by difference and in relation to the starting concentration 1% (w/v), as well as the percentage that was lost in the centrifuge residue. This residue is possibly composed of CNC agglomerates that have not been redispersed.

As a centrifugation step was performed after the redispersion of the dried nanocrystals, the recovery of these nanoparticles was calculated as the suspensions had sedimentable residues. The CNC recovery efficiency was ranging from 15.6 to 49.6% (Table 1). In addition, there was a tendency for better recovery of CNC for the dialyzed sample (35.2%) compared to the without dialysis (15.6%) sample, both without the addition of anti-binder agents. This can be explained due to the possible presence of cellulose chain fragments from the amorphous region (normally removed during the dialysis stage) that may have potentialized the formation of hydrogen bonds, promoting the formation of CNC agglomerates with greater difficulty to be redispersed. The best result was found when cationic surfactant was used as an anti-binder agent (49.6%) in comparison to glycerol (30.6%), for dialyzed suspensions, and 39.5% and 33.7%, for samples without dialysis, respectively (Table 1). In this case, the difference between the chemical agents used (glycerol, a tri-alcohol, and DTAB, a cationic surfactant), may have been responsible for the most favorable results for the surfactant. Although glycerol was used in this study as a wetting agent, it may have potentialized hydrogen bonds considering that it has three hydroxyls in its molecule. On the other hand, the surfactant may have acted to prevent the formation of these bonds, facilitating dispersion.

Table 1. Quantitative evaluation of the redispersion step of cellulose nanocrystal (CNC) suspensions after the oven-drying step

Sample	Recovery of CNC ± Sd (%)	Residue (%)
D/NA/DRY	35.20 ± 0.10	64.8
D/GLY/DRY	30.58 ± 0.05	69.4
D/DTAB/DRY	49.55 ± 0.07	50.4
ND/NA/DRY	15.60 ± 0.30	84.4
ND/GLY/DRY	33.70 ± 0.10	66.3
ND/DTAB/DRY	39.50 ± 0.20	60.5

Legend: D- with dialysis; ND- without dialysis; NA- without anti-binder agent; GLY- glycerol; DTAB- cationic surfactant; DRY- with drying.

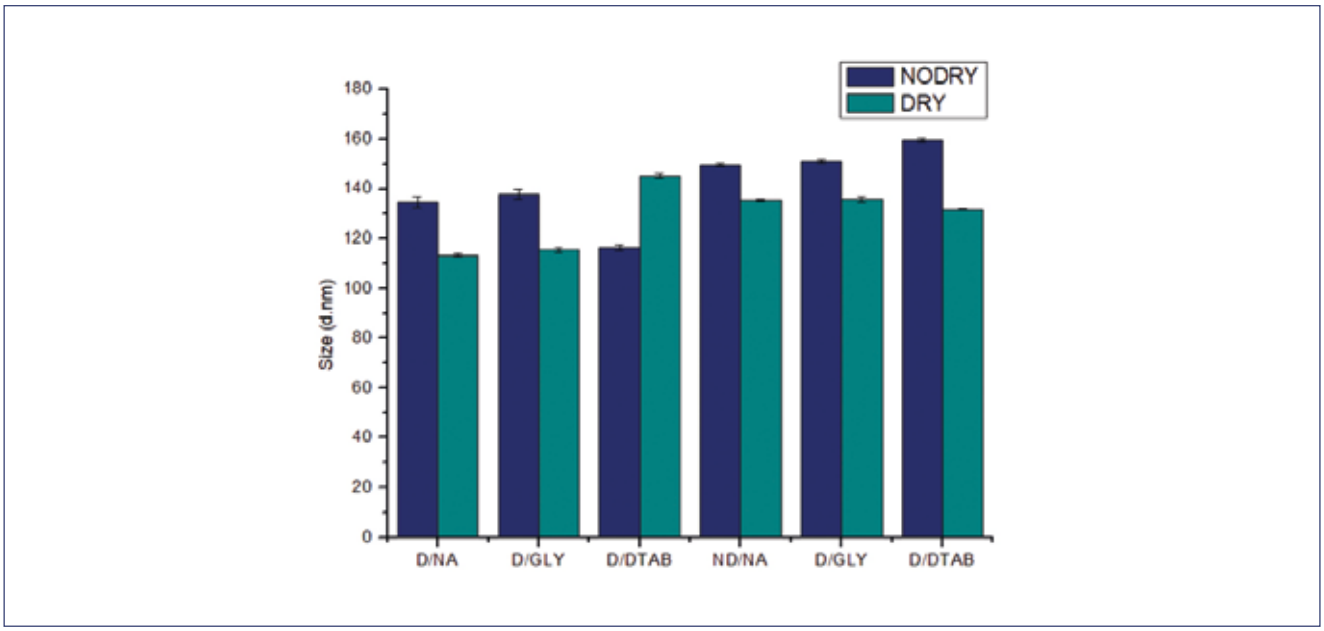

Figure 6. Dimension results of cellulose nanocrystal suspensions with drying and without drying.
Legend: D- with dialysis; ND- without dialysis; GLY- glycerol; DTAB- cationic surfactant; NA- without anti-binder agent; 08- dosage of 0.8% anti-binder agent; DRY- with drying; NO DRY- without drying.

Characterization and evaluation of the redispersion of cellulose nanocrystals after the drying step

The average equivalent diameters of nanocrystals with or without drying did not show significant differences (Figure 6). In addition, all mean-diameter values found are within the range reported in literature, as previously reported, for CNC stock suspensions. In general, there was a (non-significant) tendency for CNC from redispersed suspensions to have smaller sizes, indicating the purification allowed by centrifugation. The differences were not extensive, the error bars were calculated based on the standard deviation between all means, indicating that the concentration of values is high and the uncertainty is low, as can be seen in Figure 6.

With regard to the average values of zeta potential (Figure 7), there were also no significant differences for suspended nanocrystals, considered as stable particles.

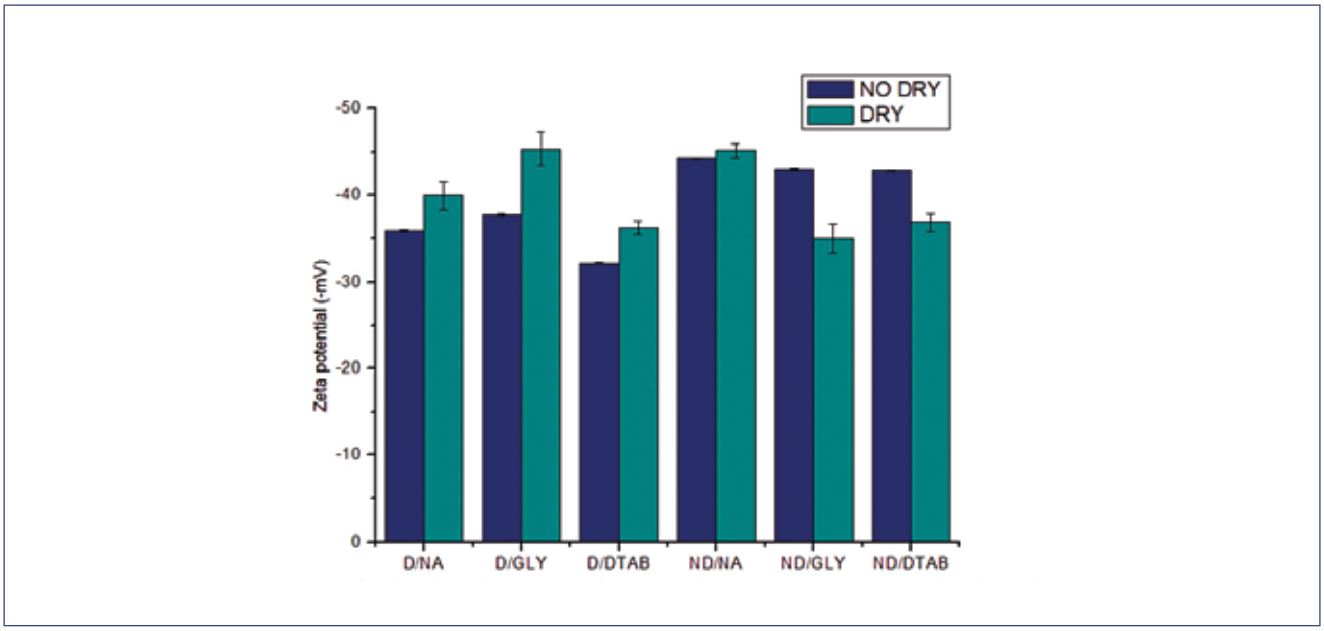

Figure 7: Average distribution of zeta potential according to whether or not drying is performed.
Legend: D- with dialysis; ND- without dialysis; GLY- glycerol; DTAB- cationic surfactant; NA- without anti-binder agent; 08- dosage of 0.8% anti-binder agent; DRY- with drying; NO DRY- without drying.

CONCLUSIONS

The main objective of this study was to evaluate the effect of dialysis on CNC suspensions and the effect of adding anti-binder agents on the redispersion of CNC suspensions after drying by evaporation in an oven, on the dimensional and surface load characteristics of these nanoparticles and on the recovery levels. According to the results achieved in this study, it can be concluded that: the dialysis stage was more favorable to the CNC recovery after drying, compared to the result achieved in the samples without dialysis, both without the addition of an anti-binder agent. In general, for the anti-binder use agents, glycerol and dodecyltrimethylammonium bromide, the cationic surfactant showed better results in both dialyzed and non-dialyzed suspensions. However, the addition of these reagents was not enough to allow for the satisfactory recovery of efficiency levels of dried CNC. For all samples, there was a residue that was not redispersed, probably formed from agglomerate CNC; the CNC drying resulted in low recovery efficiency values. However, for the recovered fractions, the results of dimensions and surface load were as expected and practically without any significant difference between different tests; an economic feasibility study is recommended in the case of adopting one or another dry CNC production route. In this case, depending on the application, the purity of the rehydrated CNC must be considered. New studies are being conducted with the aim of finding other alternatives to facilitate the redispersion of CNC after the drying step.

ACKNOWLEDGEMENTS

The authors are grateful for the financial support of FAPEMIG (Project APQ-03707-16), CNPq and PPG-UFV. To Professor Nilda de Fátima and graduate student Rafael, for the analyses carried out in the Packaging Laboratory of the Food Technology Department at UFV. To all who, directly or indirectly, contributed to the development of this study. ■

REFERENCES

1. Beck, S., Bouchard, J., Berry, R. "Dispersibility in water of dried nanocrystalline cellulose," *Biomacromolecules*, v.12, pp.1486-1494. (2012).

2. Brinchi, L., Cotana, F., Fortunati, E., Kenny, J. M. "Production of nanocrystalline cellulose from lignocellulosic biomass: technology and applications," *Carbohydrate Polymers*, v.94, num.1, pp.154-169. (2013).

3. Ditzel, F. I., Prestes, E., Carvalho, B. M., Demiate, I. M., Pinheiro, L. A. "Nanocrystalline cellulose extracted from pine wood and corncob," *Carbohydrate Polymers*, v.157, pp.1577–1585. (2017).

4. Esparza, Y., Ngo, T. D.; Fraschini, C. and Boluk, Y. "Aggregate Morphology and Aqueous Dispersibility of Spray-Dried Powders of Cellulose Nanocrystals," *Industrial and Engineering Chemistry Research*, v.58, num.43, pp.19926–19936. (2019).

5. Lee, H. J., Lee, H. S., Seo, J., Kang, Y. H., Kim, W., Kang, T. K. "State-of-the-Art of Cellulose Nanocrystals and Optimal Method for their Dispersion for Construction-Related Applications," *Applied Sciences*, v.9, pp. 426. (2019).

6. Mirhosseini, H., Tan, C.P., Hamid, N.S.A., Yusof, S. "Effect of Arabic gum, xanthan gum and orange oil contents on zeta-potential, conductivity, stability, size index and pH of orange beverage emulsion," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, v.315, num.1-3, pp.4756. (2008).

7. Peng, Y., Gardner, D. J.; Han, Y. "Drying cellulose nanofibrils: in search of a suitable method". *Cellulose*, v.19, num.1, pp.91–102, (2012).

8. Santana, M. F., Sousa, M. M., Yamashita, F. M., Moreira, B. C., Almeida, J. M., Teixeira, A. V. N., Silva, D. J. "Cellulose nanocrystal production focusing on cellulosic material pre-treatment and acid hydrolysis time," *O Papel* (São Paulo), v.80, pp.59-66. (2019).

9. Silva, D.J., D'almeida, M.L.O. "Nanocristais de celulose," *O Papel*, v.70, num.07, pp.34-52. (2009).

10. Souza Lima, M.M., Borsali, R. "Rodlike Cellulose Microcrystals: Structure, Properties, and Applications," *Macromolecules Rapid Commun*. V.25, pp.771-787. (2004).

11. Tingaut, P., Zimmermann, T., Lopez-Suevos, F. "Synthesis and characterization of bionanocomposites with tunable properties from poly (lactic acid) and acetylated microfibrillated cellulose," *Biomacromolecules*, v.11, num.2, pp.454–464. (2010).