

# Extraction of Cellulose Nanocrystals (NCC) from Cotton Waste and Morphology of NCC Obtained with Different Alkali Neutralization

## ABSTRACT

The extraction of cellulose nanocrystals (NCC) from cotton textile waste, constituted by 70% long fibers and 30% cotton linter, was performed through the action of sulfuric acid followed by solution neutralization with two different alkalis, namely ammonia and sodium bicarbonate, which yielded microcellulose (MCC), then centrifuged to NCC. The action of the two alkalis was compared as for fiber repeatability and morphology, and the results obtained using ammonia were considered more suitable for possible introduction of NCC for the repair of historical paper artifacts. This evidence was obtained by applying optical/polarized light microscopy observation and dynamic light scattering (DLS) results.

*Keywords: Cotton waste; nanocellulose extraction; alkali neutralization; Dynamic light scattering (DLS)*

## 1. INTRODUCTION

Extraction of cellulose nanocrystals (NCC) from cellulosic solid residue (CSR) represents an important way of upcycling it, therefore obtaining a material with some value, hopefully with a reasonable yield that would make the extraction worthwhile. Overtime the extraction of NCC has been performed from wastes obtained from the productive systems of different natural fibers, with the idea of operating as much as possible in conditions of circular economy, therefore using a zero waste strategy [1]. A common procedure for the purpose used involves the use of an acid solution, so to obtain hydrolysates of the waste stream: this is most frequently performed with sulfuric acid, and then neutralized using an alkaline solution [2]. Cellulosic waste stream from which NCC have been extracted includes, among others, materials from a large number of plants, in particular oil palm [3], pineapple leaves [4], Phormium tenax [5], hemp [6], okra bahmia [7], etc. In most cases the application of NCC, once extracted, has been their use as the reinforcement of polymer matrices, such as poly(vinylalcohol) (PVA) [8], etc. More recent studies have broadened even more the range of fibers, which can provide waste material for NCC extraction, with very variable yield, due to the different characteristics of plants, such as it is shown for example in [9-11].

In terms of practical use though, one of the main cellulosic products is represented by cotton, which is an abundant waste from textiles production and is basically almost pure cellulose, reaching up to 90% in weight. Cotton normally used in the textile industry is in the range recognized as medium length fibers, hence between 18 and 28 mm long. In contrast, shorter (cotton linter) and longer fibers are mostly considered as waste, therefore it can be considered suitable for the extraction of nanocellulose. In general terms, it proved effective for the purpose, whether colored or not, despite some differences in yield, in sulfonation efficiency and thermal stability [12]. More specifically, a study on the extraction of NCC from

42 cotton linter originating from Brazil did demonstrate that controlling waste stream for  
43 extraction may result in a more uniform quality product: cotton linter is particularly **adapted**,  
44 in that it does not require pulping before extraction [13].

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46 The particular aim of this study is to extract and **characterize** the morphology of cotton waste  
47 used, **which results** from discarded materials **obtained** from the development of pure  
48 cellulose paper products at a dedicated technical school in Fabriano, Italy. The idea is to  
49 possibly use the nanocellulose resulting as a material for restoration of precious ancient  
50 paper artifacts. However, the present work concentrates on the feasibility of the method and  
51 on the morphology of nanocellulose obtained using two different alkalis, namely sodium  
52 bicarbonate and ammonia.

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## 54 2. MATERIAL AND METHODS

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### 56 2.1 Extraction

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58 Crystalline nanocellulose (NCC) has been extracted starting from **a raw mixed waste**  
59 **material consisting approximately** of **100 mL of 70% long bleached fiber from cotton mass**  
60 **and 30% short fiber from cotton linter with bulk density of 0.6 g/mL**; this yielded 2.9 g of  
61 cellulose through hydrolysis with 110 ml of H<sub>2</sub>SO<sub>4</sub> 96 wt%, T = 45°C ÷ 50°C, mechanical  
62 stirring, t = 3h 45 min) followed by the addition of 600 ml of icy distilled water to stop the  
63 hydrolysis. After this, decantation for one night was performed, followed by cycles of  
64 centrifugation (7000 rpm, t = 30 min) and washing with distilled water until a neutral pH is  
65 achieved. The final stage was composed by dialysis and sonication. **The total NCC solution**  
66 **(approximately 150 ml)** obtained was characterized by **dynamic light scattering (DLS)**.

67 Two different alkalis, namely sodium bicarbonate and ammonia, were attempted to  
68 neutralize the solution, with attention to have the most repeatable and less dispersed fiber  
69 morphology. **The neutralization was carried out with sodium bicarbonate according to the**  
70 **reaction:**



72 and using ammonia according to the reaction:



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### 77 2.2 Dynamic Light Scattering (DLS)

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79 Different microscopy images have been acquired, at magnifications between x10 and x20,  
80 from an ML9000 Meiji polarized light optical microscope, performing subsequently Dynamic  
81 Light Scattering using a Malvern Zetasizer analyzer to obtain a size distribution of the fiber  
82 obtained.

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84 **Dynamic Light Scattering (DLS)** is a non-invasive technique for the measurement of the  
85 dimension of molecules, nanoparticles or colloids, at dimensions under the micron and in  
86 this specific case it has been used to measuring the hydrodynamic diameter following from  
87 diffusion measurements, according to the Stokes-Einstein equation [14]. To obtain different  
88 evaluations of the cellulose fibers sizes, for a sounder reliability of the test, three DLS  
89 measurements were carried out on a 1 ml solution. The second and the third measurements  
90 were performed after 5 and 10 minutes from the first one, respectively.

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92 Since the extraction yielded microcrystalline fibers, these underwent further to a  
93 centrifugation cycle at 7000 rpm, for 30 minutes, as reported above, in order to separate the  
94 dimensionally larger fraction from the supernatant, which constituted the nanometric fraction.

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### 3. RESULTS AND DISCUSSION

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98 After the process of sulfonation and subsequent neutralization, a microcellulose was  
99 obtained, whose characteristics are reported in Figure 1-2 (ammonia neutralization) and  
100 Figure 3-4 (sodium bicarbonate neutralization). In Figure 1 and 3 fiber distribution in a drop of  
101 solution is shown under polarized light. In the case of ammonia neutralized microcellulose  
102 fibers, a considerable part of the material extracted has similar optical properties, yielding a  
103 more uniform color over fiber surface. This indicates both that their surface is even, and that  
104 they are also mechanically more regular. Also the limited presence of detached parts from  
105 the fiber suggests the possibility of a more frequent cylindrical geometry for fibers in Figure 1  
106 than in Figure 3. Aspect ratios i.e., length/diameter of the fibers, appear to be the most  
107 various, although in general they are for both neutralization methods mostly above 10,  
108 therefore providing some prospective reinforcement effect for the introduction in a polymer  
109 matrix, such as e.g., poly(vinylalcohol) (PVA) [15].

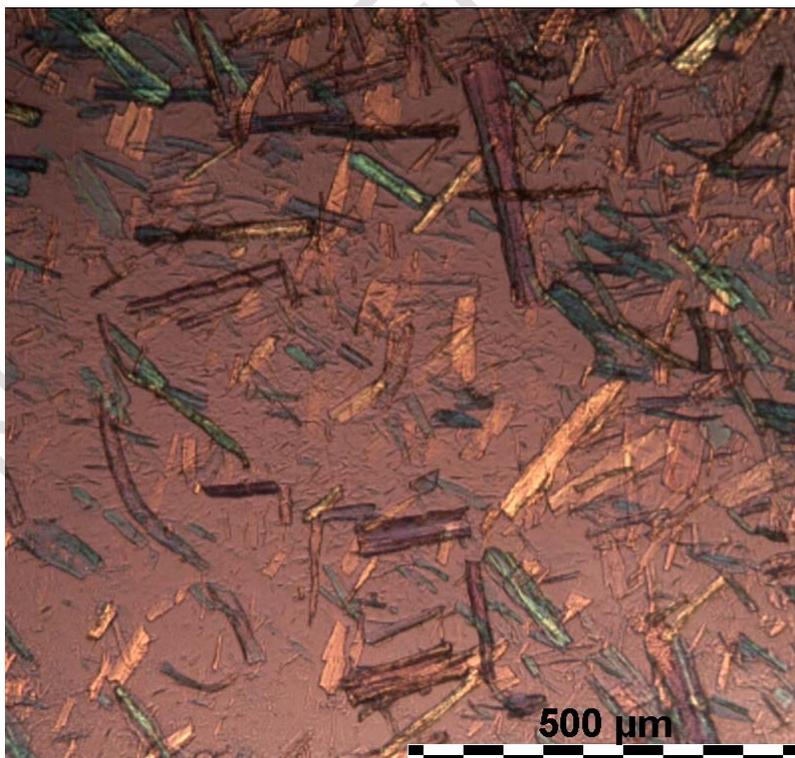
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111 In Figure 2 and 4 some isolated fibers are depicted under normal light. In this case, striations  
112 were in particular observed in the micrographs, which are an indication that orientation of the  
113 filaments occurred, producing material with fibrillar morphology. This would lead as a result  
114 to a higher effect of tensile reinforcement for the microfibril, provided filaments not tend to be  
115 at an angle or detach from the bulk of the fiber, a case which is termed as "fibrillation" and  
116 leads to more mechanical inconsistency [16]. Fibrillation appears more frequent with the  
117 sodium bicarbonate neutralized fibers in Figure 4.

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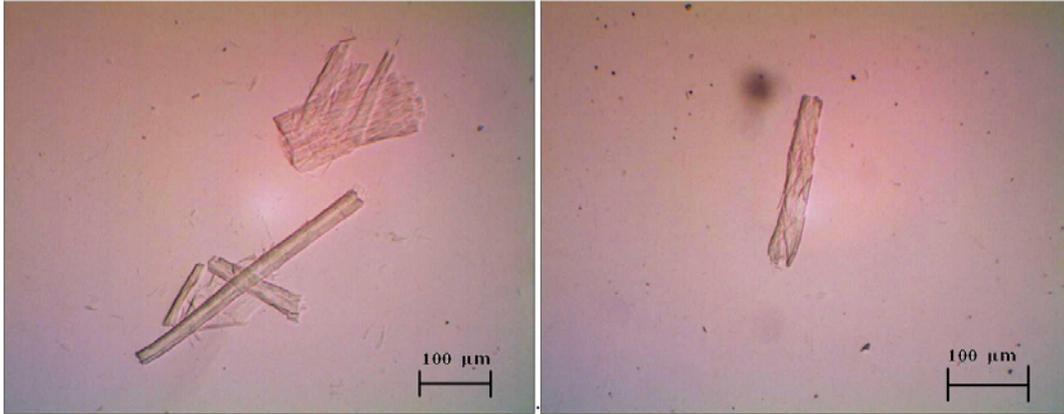


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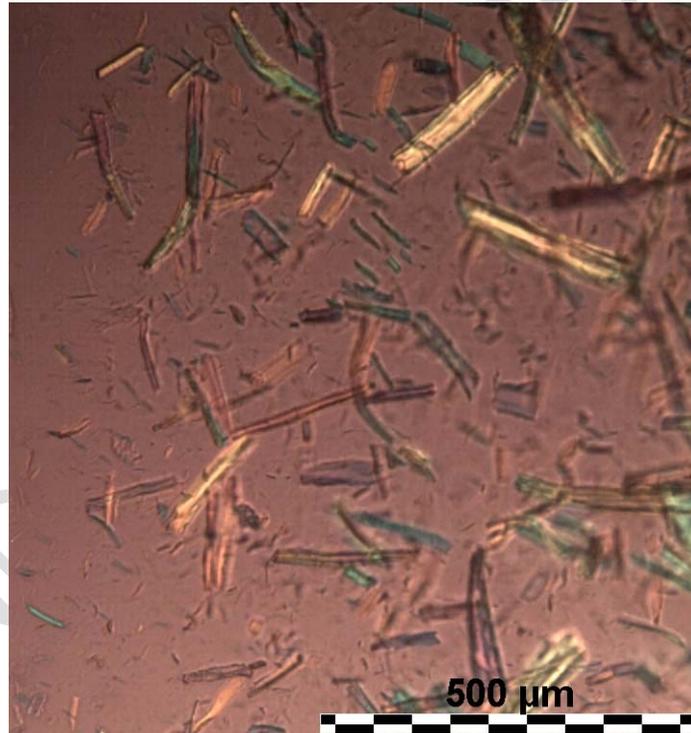
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**Fig. 1. Optical polarized light micrograph of cellulose extracted using  $\text{NH}_3$  neutralization, before centrifugation**



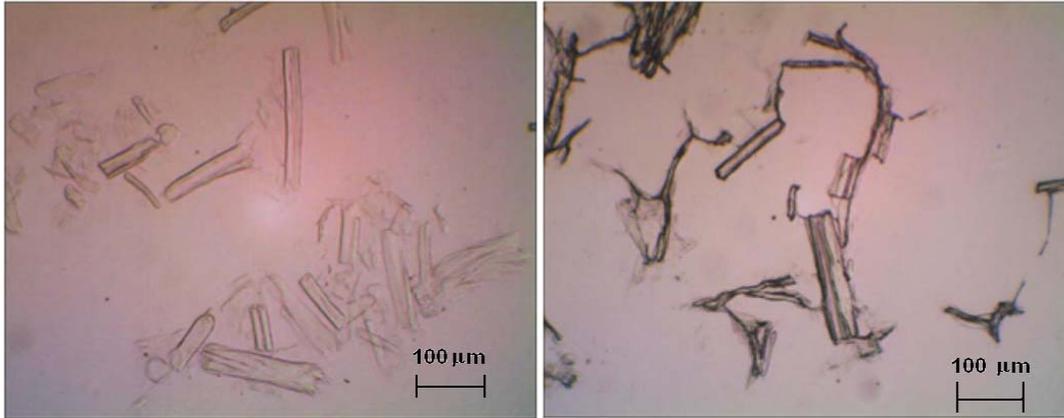
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**Fig. 2. Optical micrograph of cellulose extracted using  $\text{NH}_3$  neutralization, before centrifugation**



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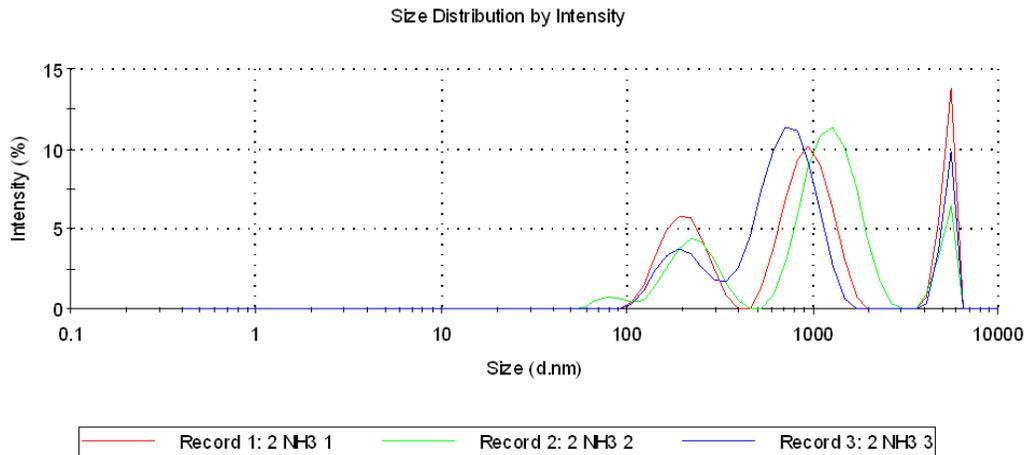
**Fig. 3 Optical polarized light micrograph of cellulose extracted using  $\text{NaHCO}_3$  neutralization, before centrifugation**



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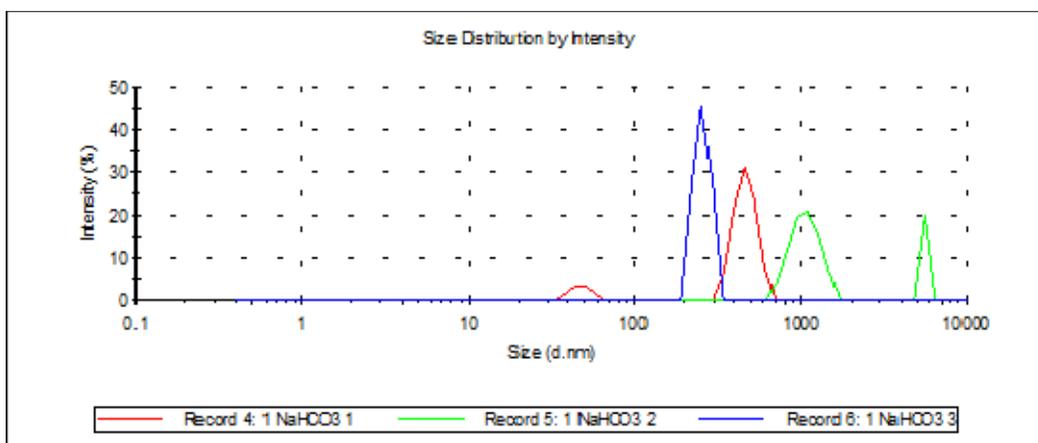
**Fig. 4 Optical micrograph of cellulose extracted using  $\text{NaHCO}_3$  neutralization, before centrifugation**

The distribution of the fibers, as from DLS graph, did appear to present a number of peaks and also the three measurements on the same solution did not appear to be superposed, which suggests a scarce reliability of the measure, for neutralization with both alkalis (Figure 5 for ammonia and 6 for sodium bicarbonate). This is considerably worsened in the case of neutralization with sodium bicarbonate, where the peaks revealed do not appear having any real correspondence in the three tests carried out.



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**Fig. 5. DLS distribution of cellulose extracted using  $\text{NH}_3$  neutralization, before centrifugation**



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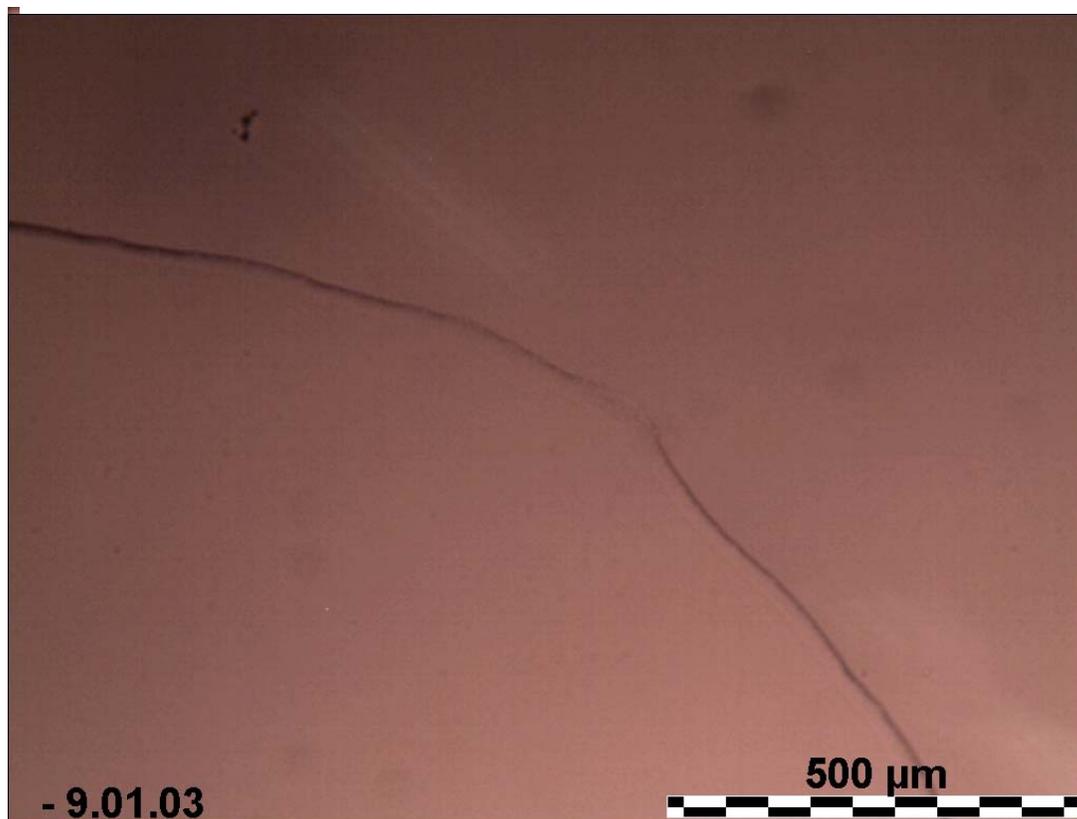
**Fig. 6 DLS distribution of cellulose extracted using NaHCO<sub>3</sub> neutralization, before centrifugation**

As it is possible to notice in Figure 7, referred to ammonia-extracted fibers, the fibers obtained after centrifugation are of nanometric dimension and therefore not apparent in the optical microscope image at 20x magnification.

After centrifugation, the evaluation carried out using DLS confirm the superiority of ammonia neutralization also in the case of NCC, since the dimensions appear more repeatable and less scattered with a statistical mode consistently in the region of 500 nm (Figure 8). In contrast, in the case of sodium bicarbonate neutralization, it has been observed that the above statistical mode is only clearly indicated in one of the three measurements, in the other cases the values are still quite dispersed and confused (Figure 9).

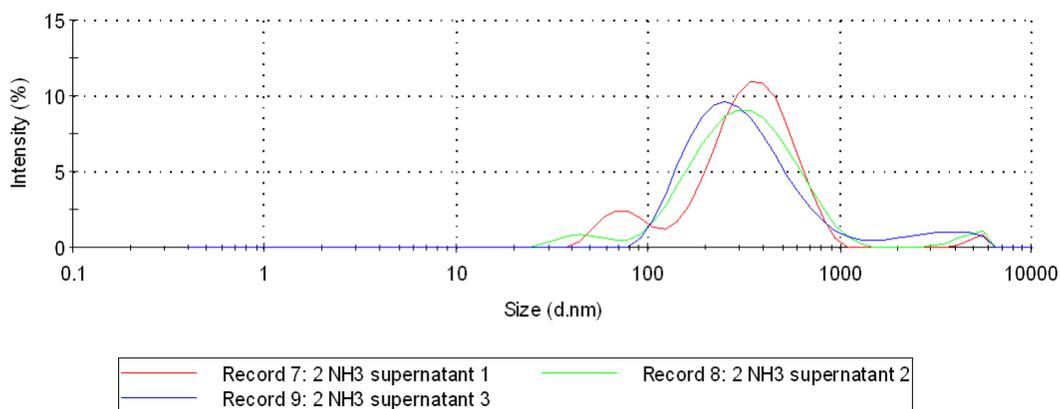
UNDER REVIEW

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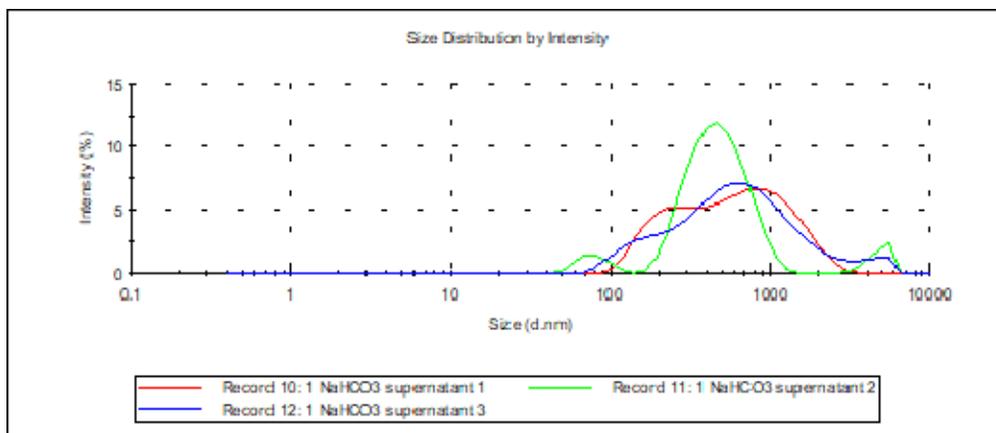
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**Fig. 7. Micrograph of cellulose extracted using NH<sub>3</sub> neutralization.**



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**Fig. 8. DLS distribution of cellulose extracted using NH<sub>3</sub> neutralization, after centrifugation**



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**Fig. 9 DLS distribution of cellulose extracted using NaHCO<sub>3</sub> neutralization, after centrifugation**

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#### 4. CONCLUSION

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The extraction of cellulose nanocrystals (NCC) from cotton textile waste (70% long fibers and 30% cotton linter) through the action of sulfuric acid followed by solution neutralization with two different alkalis, namely ammonia and sodium bicarbonate proved effective in general terms. This yielded microcellulose (MCC) of good quality and uniformity, although in the latter case the fibers were thinner and of less regular shape than in the former one. A subsequent action of centrifugation led to obtaining NCC. Comparing the action of the two neutralizing alkalis, the materials obtained using ammonia **can be** considered superior. The evidence provided by optical/polarized light microscopy observation and dynamic light scattering (DLS) results suggested a higher geometrical regularity and fibrillary adhesion, together with a lower dimensional dispersion with respect to those yielded by applying a sodium bicarbonate neutralization. **The result of this study, hence the superiority of ammonia for the neutralization process, is considered of interest to prepare the procedure of extraction for the introduction of NCC for the repair of historical paper artifacts.**

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#### COMPETING INTERESTS

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Authors have declared that no competing interests exist.

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