

# 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 (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, as from the evidence obtained from 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 with a reasonable yield a material with some value. This extraction has been performed from wastes obtained from the productive systems of different natural fibers, with the idea of operating these 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 biopolymer matrices, such as poly(vinylalcohol) (PVA) [8], etc.

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, whereas shorter (cotton linter) and longer fibers are mostly considered as waste, therefore it can be considered suitable for the extraction of nanocellulose. In practical terms, it proved effective for the purpose, whether colored or not, despite some differences in yield, in sulfonation efficiency and thermal stability [9]. More specifically, a study on the extraction of NCC from cotton linter originating from Brazil did demonstrate that controlling waste stream for extraction may result in a more uniform quality product: cotton linter is particularly suitable, in that it does not require pulping before extraction [10].

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

## 2. MATERIAL AND METHODS

### 2.1 Extraction

Crystalline nanocellulose (NCC) has been extracted starting from a solution of 70% long bleached fiber from cotton mass and 30% short fiber from cotton linter; 200 ml sodium hypochlorite yielded 2.9 g of cellulose through hydrolysis (110 ml of H<sub>2</sub>SO<sub>4</sub> 96 wt%, T = 45°C ÷ 50°C, mechanical stirring, t = 3h 45 min) followed by the addition of 600 ml of icy distilled water to stop the hydrolysis. After this, decantation for one night was performed, followed by cycles of centrifugation (7000 rpm, t = 30 min) and washing with distilled water until a neutral pH is achieved. The final stage was composed by dialysis and sonication. The NCC solution (150 ml) obtained was characterized by DLS.

Two different alkalis, namely sodium bicarbonate and ammonia, were attempted to neutralize the solution, with attention to have the most repeatable and less dispersed fiber morphology. The neutralization was carried out with sodium bicarbonate according to the reaction  $2\text{NaHCO}_3 + \text{H}_2\text{SO}_4 \leftrightarrow \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{CO}_3$  and using ammonia according to the reaction  $2\text{NH}_3 + \text{H}_2\text{SO}_4 \leftrightarrow (\text{NH}_4)_2\text{SO}_4$

### 2.2 Dynamic Light Scattering (DLS)

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

Dynamic Light Scattering (DLS) is a non-invasive technique for the measurement of the dimension of molecules, nanoparticles or colloids, at dimensions under the micron. IN DLS the sample is illuminated using a Laser, and the variation of light intensity are measured over time. The variations of intensity measured by the detector are generated from the Brownian movement of particles that originates the scattering. This means that, being equal the temperature and the viscosity, the small particles move more rapidly, creating fast variations of scattering intensity, whereas the large particles moves more slowly, with subsequent slow intensity variations. Owing to the use of a self-correlator, the velocity of intensity variations is measured and the coefficient of diffusion for particles is calculated from its correlation function. Stokes-Einstein equation allows then converting the diffusion coefficient in a hydrodynamic diameter. Three DLS measurements were carried out on a 1 ml solution, the second and the third after 5 and 10 minutes from the first one, respectively.

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

93 **3. RESULTS AND DISCUSSION**

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95 After the process of sulfonation and subsequent neutralization, a microcellulose was  
96 obtained, whose characteristics are reported in Figure 1-2 (ammonia neutralization) and  
97 Figure 3-4 (sodium bicarbonate neutralization). In Figure 1 and 3 fiber distribution in a drop of  
98 solution is shown under polarized light. In the case of ammonia neutralized microcellulose  
99 fibers there are more of these that have similar optical properties, yielding a more uniform  
100 color over their surface. This indicates both that their surface is even, and that they are also  
101 mechanically more regular. Also the limited presence of detached parts from the fiber  
102 suggests the possibility of a more frequent cylindrical geometry for fibers in Figure 1 than in  
103 Figure 3. Aspect ratios i.e., length/diameter of the fibers, appear to be the most various,  
104 although in general they are for both neutralization methods mostly above 10, therefore  
105 providing some prospective reinforcement effect for the introduction in a polymer matrix,  
106 such as e.g., poly(vinylalcohol) (PVA) [11].

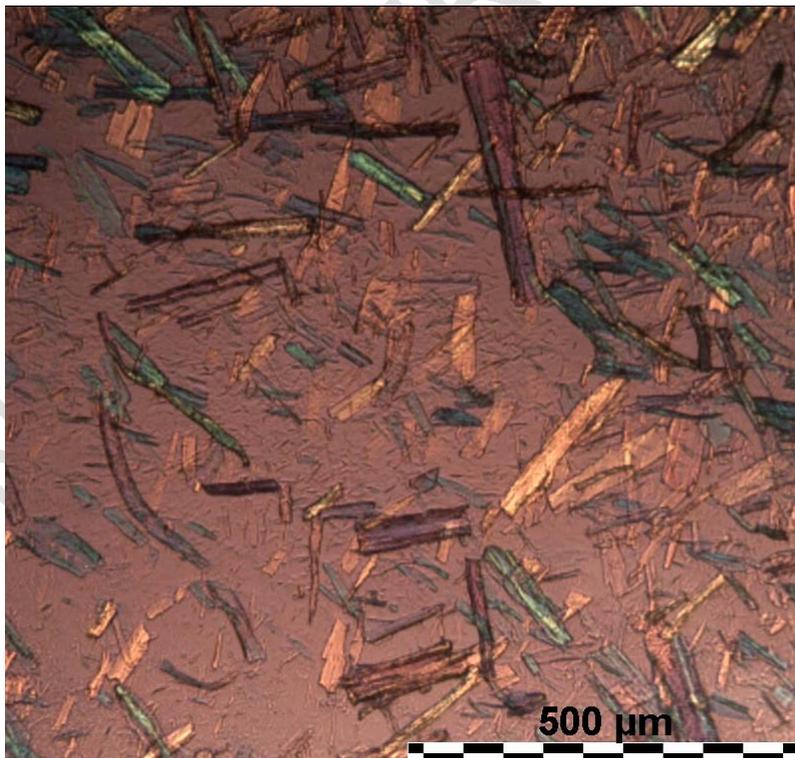
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108 In Figure 2 and 4 some isolated fibers are depicted under normal light. In this case, striations  
109 were in particular observed in the micrographs, which are an indication that orientation of the  
110 filaments occurred, producing a fibrillar morphology. This would lead as a result to a higher  
111 effect of tensile reinforcement for the microfiber, provided filaments not tend to be at an  
112 angle or detach from the bulk of the fiber, a case which is termed as “fibrillation” and leads to  
113 more mechanical inconsistency [12]. Fibrillation appears more frequent with the sodium  
114 bicarbonate neutralized fibers in Figure 4.

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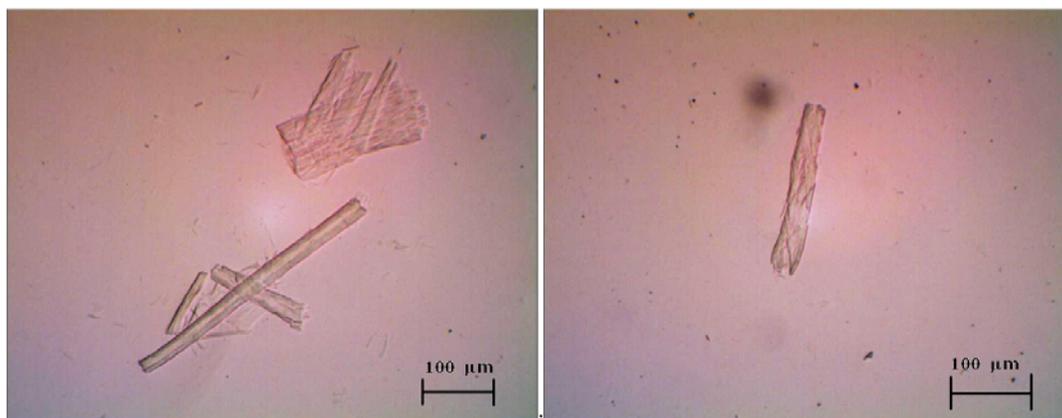
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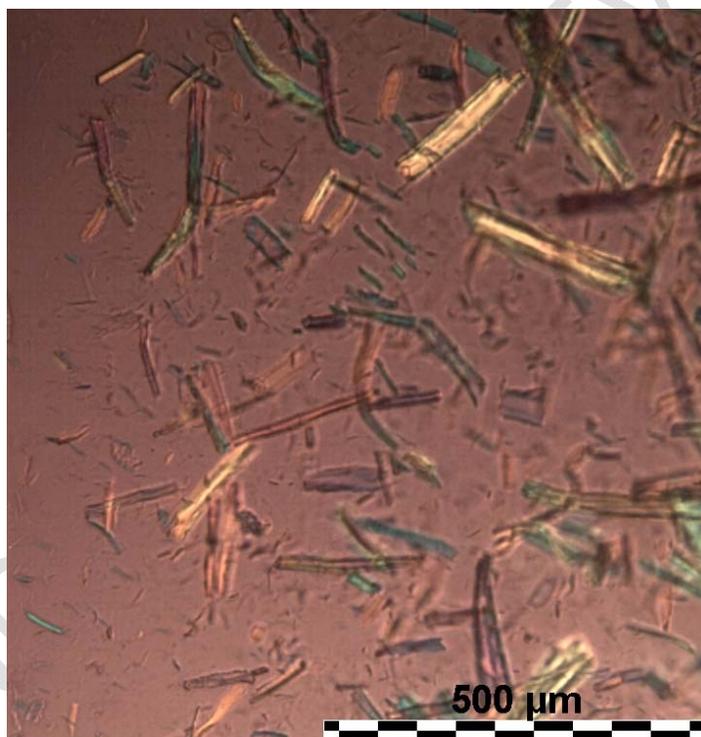
**Fig. 1. Optical polarized light micrograph of cellulose extracted using NH<sub>3</sub> neutralization, before centrifugation**

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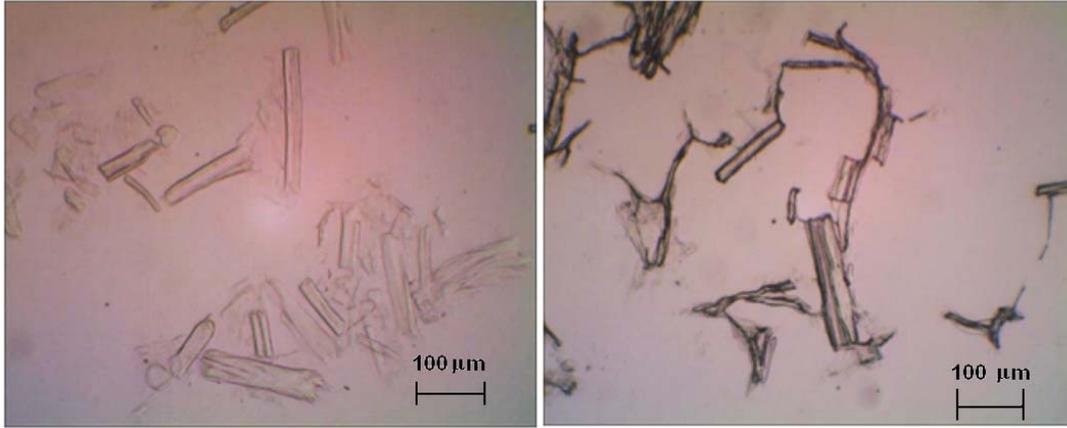
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**Fig. 2. Optical micrograph of cellulose extracted using NH<sub>3</sub> neutralization, before centrifugation**



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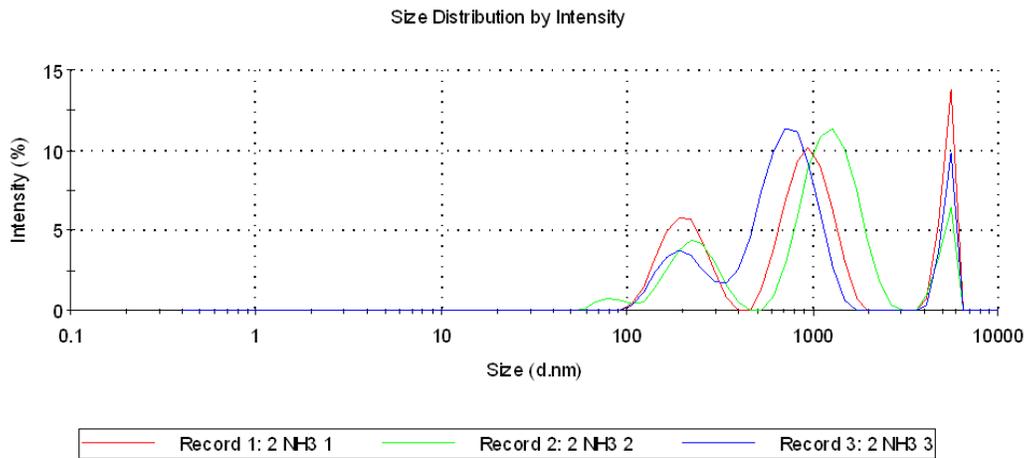
**Fig. 3 Optical polarized light micrograph of cellulose extracted using NaHCO<sub>3</sub> neutralization, before centrifugation**



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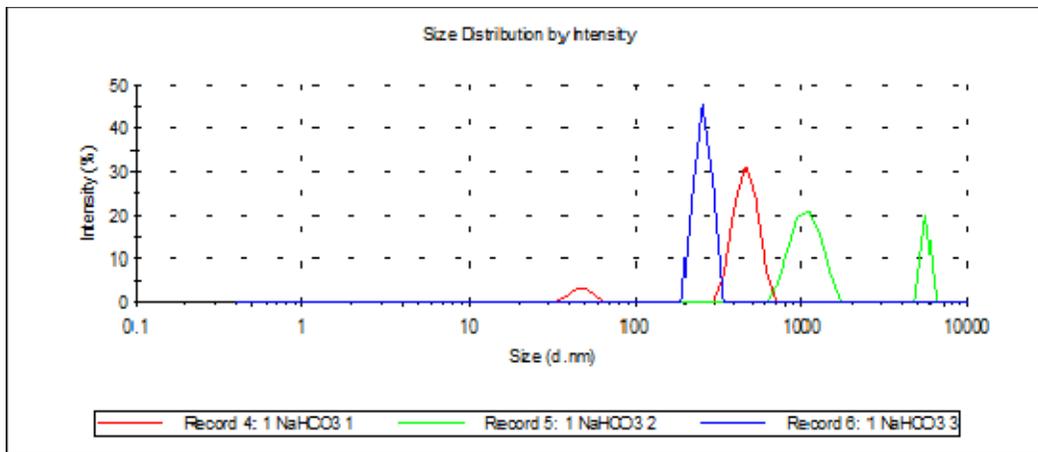
**Fig. 4 Optical micrograph of cellulose extracted using  $\text{NaHCO}_3$  neutralization, before centrifugation**

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 worst in the case of neutralization with sodium bicarbonate, where the peaks revealed have not any sort of 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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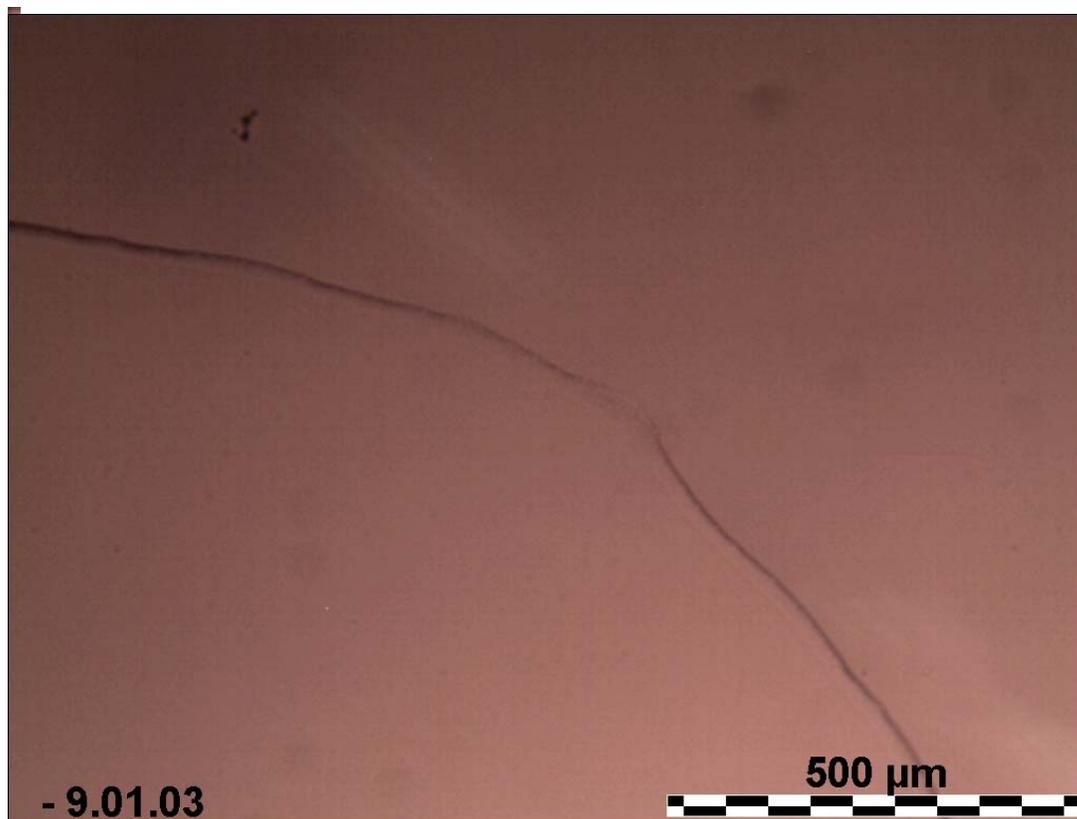
**Fig. 6 DLS distribution of cellulose extracted using NaHCO<sub>3</sub> neutralization, before centrifugation**

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 out of three measurements, in the other cases the values are still quite dispersed and confused (Figure 9).

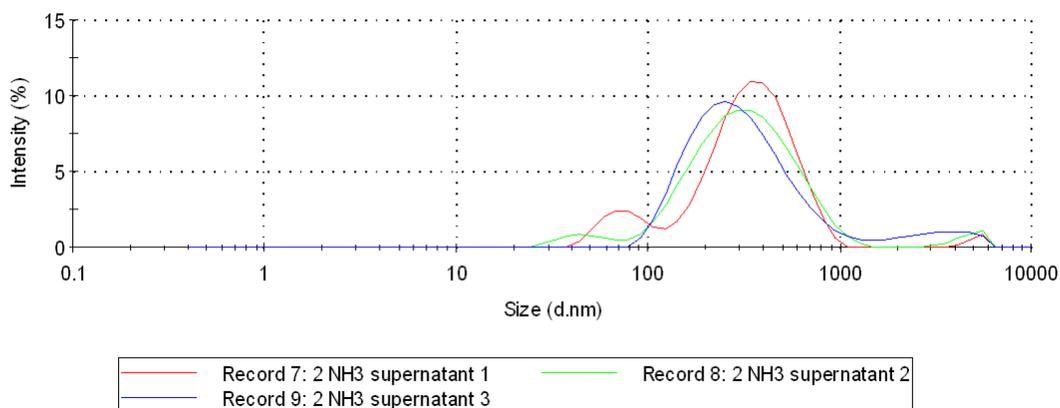
UNDER PREPARATION

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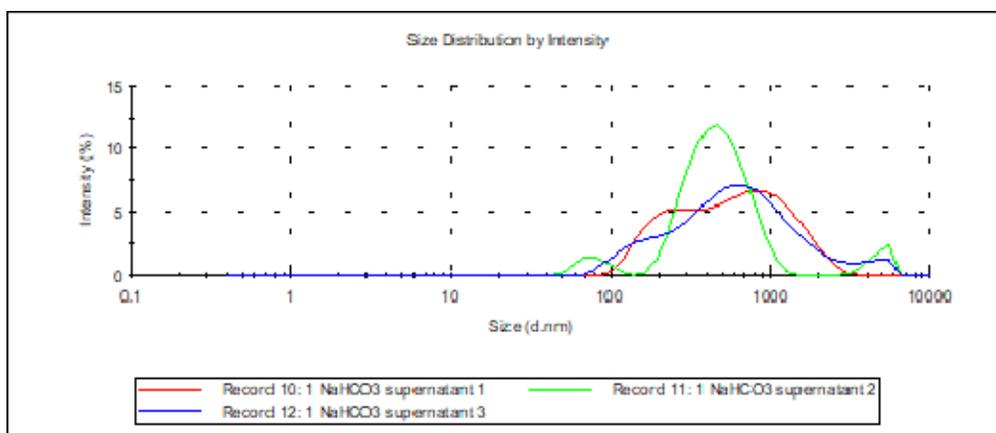
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**Fig. 7. Micrograph of cellulose extracted using NH<sub>3</sub> neutralization, proving the material yielded is of nanometric dimension**



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



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

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#### 184 **4. CONCLUSION**

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186 The extraction of cellulose nanocrystals (NCC) from cotton textile waste (70% long fibers  
187 and 30% cotton linter) through the action of sulfuric acid followed by solution neutralization  
188 with two different alkalis, namely ammonia and sodium bicarbonate proved effective in  
189 general terms. This yielded microcellulose (MCC) of good quality and uniformity, although in  
190 the latter case the fibers were thinner and of less regular shape than in the former one. A  
191 subsequent action of centrifugation led to obtaining NCC. Comparing the action of the two  
192 neutralizing alkalis, the materials obtained using ammonia were considered superior. The  
193 evidence provided by optical/polarized light microscopy observation and dynamic light  
194 scattering (DLS) results suggested a higher geometrical regularity and fibrillary adhesion,  
195 together with a lower dimensional dispersion with respect to those yielded by applying a  
196 sodium bicarbonate neutralization. This result could be exploited when disposing protocol for  
197 the possible introduction of NCC for the repair of historical paper artifacts.

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#### 200 **COMPETING INTERESTS**

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202 Authors have declared that no competing interests exist.

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