

Article

Development of Cotton Linter Nanocellulose for Complexation of Ca, Fe, Mg and Mn in Effluent Organic Matter

Vinícius de Jesus Carvalho de Souza ¹, José Cláudio Caraschi ^{1,2}, Wander Gustavo Botero ³ ,
Luciana Camargo de Oliveira ⁴  and Danielle Goveia ^{1,2,*} 

¹ Campus of Itapeva, São Paulo State University (UNESP), São Paulo 18409-010, Brazil; viniciusjcsouza@gmail.com (V.d.J.C.d.S.); j.caraschi@unesp.br (J.C.C.)

² Faculty of Pharmaceutical Sciences, Highway Araraquara-Jaú, São Paulo 14800-903, Brazil

³ Institute of Chemistry and Biotechnology, Federal University of Alagoas (UFAL), Maceió 57072-970, Brazil; wanderbotero@gmail.com

⁴ Department of Physics, Chemistry and Mathematics, Graduate School of Biotechnology and Environmental Monitoring, Federal University of São Carlos (UFSCar), Rodovia João Leme dos Santos, SP-264, São Paulo 18052-780, Brazil; lcamargo@ufscar.br

* Correspondence: danielle.goveia@unesp.br

Abstract: Effluent organic matter (EfOM) is present in different domestic and industrial effluents, and its capacity to hold metallic ions can interfere in the wastewater treatment process. Due to the low quality of water, new sustainable technologies for this purpose have become extremely important, with the development of renewable-source nanomaterials standing out in the literature. Nanocellulose (NC) deserves to be highlighted in this context due to its physicochemical characteristics and its natural and abundant origin. In this context, the interactions between NC extracted from cotton linter, organic matter fraction (humic substances) and metal ions have been evaluated. Free metal ions (Ca, Fe, Mg and Mn) were separated by ultrafiltration and quantified by atomic absorption spectrometry. The nanomaterial obtained showed potential for the treatment of effluents containing iron even in the presence of organic matter. The probable interaction of organic matter with NC prevents the efficient removal of calcium, magnesium and manganese. For these elements, it is desirable to increase the interaction between metal and NC by modifying the surface of the nanomaterial.

Keywords: aquatic humic substances; nanomaterials; metallic ions; water; bioavailability



Citation: de Jesus Carvalho de Souza, V.; Caraschi, J.C.; Botero, W.G.; de Oliveira, L.C.; Goveia, D. Development of Cotton Linter Nanocellulose for Complexation of Ca, Fe, Mg and Mn in Effluent Organic Matter. *Water* **2021**, *13*, 2765. <https://doi.org/10.3390/w13192765>

Academic Editors: Cristina Palet and Julio Bastos-Arrieta

Received: 2 September 2021

Accepted: 28 September 2021

Published: 06 October 2021

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1. Introduction

Dissolved organic matter (DOM) is the dominant form of organic matter in aquatic systems. It consists of dissolved molecules as well as aggregates of molecules. These aggregates can be seen as colloids and are very heterogeneous. The main constituents of DOM are the humic substances (HS). As they are complex mixtures of organic compounds with relatively unknown structures, they are operationally defined according to their isolation procedure [1]. The IHSS (International Humic Substances Society) advises the isolation of humic substances from water by adsorption on an XAD-8 column, at pH 2, followed by elution with sodium hydroxide solution. Humic substances are produced from the degradation of biomass and, therefore, are natural compounds present in all environments.

However, the discharge of industrial and municipal effluents may introduce humic materials and humic precursors into surface waters, denominated humic-like substances [2]. Effluent organic matter (EfOM) is characterized by the combination of natural organic matter (NOM), the particulate material in suspension associated with microbial products, and trace harmful chemicals. Most NOM comes from water and is the main component of wastewater. This material, in general, is not considered a toxic pollutant; however, the EfOM can significantly contribute to effluent treatment processes, such as the obstruction of membranes, the limited reuse of wastewater, or the association with other compounds.

Humic substances have abundant functional groups, mainly carboxylic, carbonyl and phenolic, which confer a high capacity for complexation with metallic ions. Because of these interactions, humic substances have an important effect that need to be considered in wastewater treatment processes [3].

Interactions with nutrients and metal ions substantially affect the biogeochemical cycles of these elements, as they are not degraded, remaining in the environment for long periods of time [4]. Even metals considered essential and fundamental for animal and plant metabolisms may pose a risk to the development of the living being in situations of high or prolonged exposure.

Thus, the treatment of wastewater containing metals remains an important issue to be resolved, considering the presence of humic-like substances. There is a growing need to develop methodologies that involve solutions with low environmental impact, where nanotechnology and the use of materials from renewable sources have been highlighted. Tom [5] brought in a detailed review presenting the possible uses of nanotechnology in the field of sustainable water treatment, noting that nanotechnology has great potential in the field of sustainable water treatment and that concerns about the potential toxicity of nanomaterials themselves can be resolved by the use of natural and carbon-based nanomaterials with low toxicity. Natural nanomaterials and biopolymers, with their unique properties, high efficiency, cost-effectiveness and eco-friendly, are considered a good choice for water treatment, especially biobased nanomaterials in cellulose.

Cellulose is a macromolecule responsible for providing some of the important characteristics of plant cells, combining high mechanical strength and low density with good flexibility [6]. All these properties, combined with the fact that cellulose is a non-toxic, renewable and biodegradable material, have caused a great increase in the scientific interest in this material.

When the cellulose macromolecule is broken into nanofibers, its properties are greatly enhanced, in addition to increasing its surface area, making the material attractive for obtaining new composites. Nanocellulose (NC) has high resistance, low specific gravity, a non-abrasive nature, no toxicity, biocompatibility and biodegradability [7]. These characteristics mean NC is a material that is widely used in applications and produced on a large scale.

Thus, for the application of nanocellulose in the removal of metallic ions from wastewater containing organic matter, a very important point to be studied is how this nanomaterial will interact in EfOM and its components, such as metallic ions. It is essential to perform studies on the interactions between metal and organic matter and nanocellulose.

Organic matter plays an important role in the balance of the aquatic system, since its macromolecules, composed of complex aromatic rings and functional groups, allow the absorption of metals and other pollutants, preventing them from being absorbed by living organisms [8]. In this sense, nanomaterials can interact in these systems, causing some type of change in this absorption mechanism due to their small size and differentiated physical-chemical properties. One way to study the interactions between metal ions and natural organic matter is using aquatic humic substances in controlled conditions.

In this context, it is possible to elaborate three hypotheses for the interaction mechanism of NC with the aquatic system: EfOM can complex metals, preventing them from being absorbed by living organisms in a competition process with the nanomaterial. NC can adsorb these metals in a competitive process, increasing their lability or even serving as a transport route for metals into the cells of living organisms. Alternatively, NC can cause changes in the complexing sites of EfOM, decreasing their complexing capacity and releasing the labile metal and bioavailable material into the aquatic system.

To assess the hypotheses presented, it is necessary to study the speciation and distribution of metals in the environment using models that simulate natural conditions. One of the biggest challenges in the speciation analysis of metal ions is in the development of an analytical procedure capable of maintaining the chemical balance of a natural system.

Therefore, it is essential to develop methods to avoid undesirable disturbances in the aquatic system under study [9].

Tangential flow ultrafiltration is a method that has shown good results in differentiating complexes (EfOM + metals) from free metals in aquatic systems. This method consists of using a membrane that allows only the passage of ions, while the larger molecules of organic matter, as well as the EfOM + metal complexes and the NCs and their complexes, are retained in the system. The filtered solution corresponds to the fraction of free metals. Knowing the initial fraction of the solution and the total metals, it is possible to determine the fraction of complexed metals by the difference between total metals and free metals (filtered). The fraction of free metals present in the filtered solution can be determined using spectrometric methods [9,10]. In this sense, the objective of this work is to evaluate the interaction mechanisms between the NC and the metal complexation system (Ca, Fe, Mg and Mn) in the presence or absence of the organic matter, using HS in concentration-controlled experiments.

2. Materials and Methods

2.1. Bleaching Process and Prehydrolysis of the Cotton Linter

The NC used in this study was obtained from cotton linter (*Gossypium hirsutum*). The linter underwent acid prehydrolysis with hydrochloric acid (HCl) at a concentration of 0.3 mol L^{-1} , a temperature of 123°C and a pressure of 2.3 kg cm^{-2} . The treatment was performed in a PHOENIX AV-30 model. The ratio of linter cellulose to acid was 1:20 (g linter: mL of acid). The treatment time was 60 min, which was required for the autoclave to reach the specified conditions, followed by another 30 min of cooking at constant temperature and pressure. After the hydrolysis process, the samples were filtered, separating the solid material (prehydrolyzed linter) from the liquor. The filtering process was carried out until the liquor reached a neutral pH.

The prehydrolyzed material underwent a bleaching process based on the holocellulose content determination procedure proposed by Lamaming [11]. For 4.00 g of sample, 140 mL of distilled water, 3 mL of glacial acetic acid, 3.3 g of sodium chlorite and 4.3 g of sodium acetate were used. The reaction medium was placed in a thermostatic bath at 70°C . After 30 min from the start of treatment, a second addition of reagents (excluding water) was made, maintaining the reaction for another 60 min. At the end of the 90 min process, the samples were filtered, washed with distilled water until reaching a neutral pH and the total removal of chlorine dioxide (yellow in color), and then placed in the oven at $105 \pm 3^\circ\text{C}$ for drying.

2.2. Preparation of Nanomaterial

To obtain the NC, an adaptation of the procedure proposed by Orts et al. [12] with 1:10 sulfuric acid 64% *w/w* (pulp (g):acid (mL)) was used for the acid hydrolysis of the pulp. The temperature of this process was 60°C (temperature maintained by a hot plate); the hydrolysis time was 30 min. At the end of the process, 100 g of ice was added and the sample was decanted for 24 h. After decanting, the supernatant was discarded, while the rest went on to the centrifugation process. Centrifugation was performed in 4 cycles of 5 min, and at the end of each cycle the supernatant was discarded for the addition of water.

After centrifugation, the dialysis process was carried out using a 21 mm diameter SERVAPOR membrane. Before use, preparation was necessary, as the membrane contains substances with traces of heavy metals ($<50 \text{ ppm}$) that prevent it from drying out. One of the procedures suggested by the manufacturer to remove these substances is to heat the membrane in metal-free water at a temperature between 70 and 80°C for 2 h, stirring occasionally. The procedure is repeated three times, allowing the water to decant in each repetition.

After removing the metals, the NC solutions obtained were inserted into the membrane, attaching the ends with appropriate clips. The set was inserted into 10 L of deionized

water. Changes were made to the water in the set until the water in the container reached a neutral pH.

The characterization of the NC was made by high-resolution electron microscopy (SEM-FEG) using the high-resolution field-emission electron microscope (MEV-FEG), brand JEOL, model JSM-7500 F. The samples were previously dehydrated and mounted directly in stubs, and then metallized in a BAL-TEC® coating system (model SCD-50). The distance between the target and the sample was maintained at 50 mm for all carbon deposits. During deposition, the vacuum was maintained at 0.2 mbar. A conductive carbon layer is generally necessary to reduce the effect of the electric charge on the surface caused by the interaction between the electron beam and the sample, which can result in image distortion [13].

2.3. Effluent Organic Matter (EfOM) Simulation with Humic Substances (HS)

Effluent organic matter (EfOM) was simulated using humic substances. The HS was extracted with 100 L of water collected from the Juréia River in the city of São Sebastião, São Paulo, Brazil. The extraction was carried out using the methodology adopted by most researchers associated with the International Humic Substances Society (IHSS), using DAX-8 superlite microporous resin [14]. The EfOM was simulated using deionized water, mass of extracted HS (powder) and pH adjustments to 5.5.

2.4. Evaluation of the Interaction of NC with Metals

The verification of the interaction of NC with metallic ion was carried out by preparing the initial solutions of Fe (II)/Mn (II) and Ca (II)/Mg (II) with approximately 2 mg L⁻¹. The pH of the solutions was adjusted to 5.5 in order to approach the pH of natural water, bringing the system closer to real conditions. The NC suspension were added (50–1200 µL) into 250 mL of the multielementar solution. After a period of 24 h (period for the formation of metal-nano complexes) the tangential flow ultrafiltration process was carried out.

The tangential ultrafiltration system used is composed of a peristaltic pump, tygon tubes and a porosity membrane of 1 kDa and 47 mm in diameter. To carry out the filtration, pressure controllers were used, so that when the aliquots were collected, the free metals were separated from the metals complexed to NC. The concentrations of free ions were determined according to item 2.7.

2.5. Evaluation of the Influence of NC on the Metal-EfOM Complexes

Into 200.0 mL of EfOM 100 mg L⁻¹ solution, 2 mg L⁻¹ of the metals Ca, Fe, Mg and Mn were added, and the pH was adjusted to 5.5 to approximate the pH of natural waters. A sample of the solution was collected to determine the exact concentration of the metal in the solution (total metal). After the 24 h period, the tangential ultrafiltration of the solution was performed to determine the free metals not complexed with organic matter, before adding NC (time 0 min).

The NC (300 µL) was then added, and samples of the filtrate were collected from time to time over the 24 h period. The free metals, separated by means of the tangential flow ultrafiltration process, were quantified using the atomic absorption spectrometer (Figure 1). The concentration of complexed metals was evaluated using Equation (1).

$$\text{Complexed metal} = \text{Total Metal} - \text{Free Metal} \quad (1)$$

The Figure 1 represents all the steps described in this section.

2.6. Evaluation of the Influence of EfOM on Metal—NC Complexes

Solutions were prepared with the metals at a concentration of 2 mg L⁻¹, and 300 µL of the suspension containing NC was added. This mixture was left to stand for a period of 24 h to form metal—NC bonds. A sample was collected to quantify the total metal present in each solution, the tangential ultrafiltration process was performed, and then EfOM was added at a concentration of 100 mg L⁻¹. Aliquots of the filtrate were collected from time to time during the 24 h period.

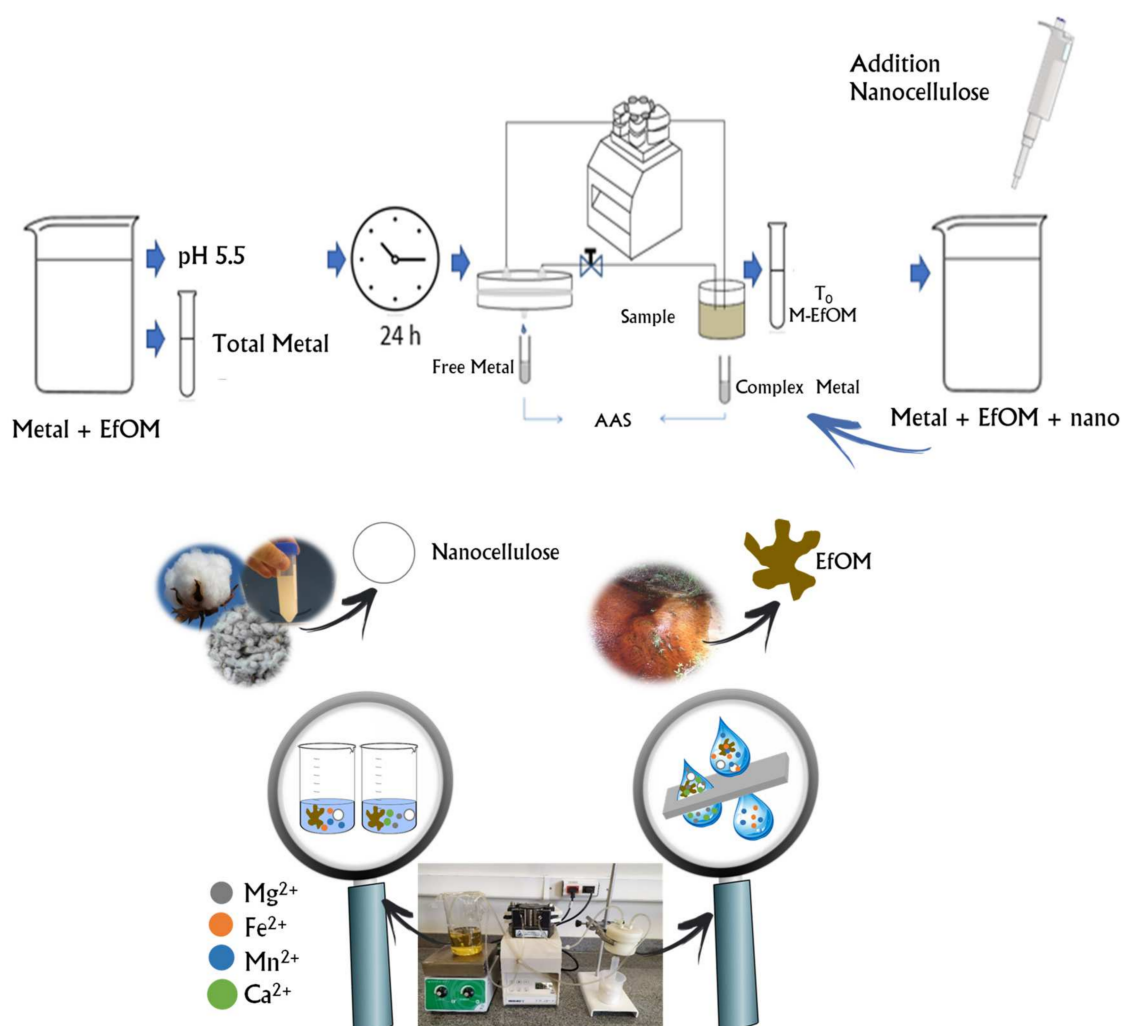


Figure 1. Ultrafiltration system used to evaluate the influence of effluent organic matter in the removal of metals from aquatic systems by nanocellulose. AAS—atomic absorption spectroscopy; EfOM—effluent organic matter; M—metal.

2.7. Determination of Metal Concentration

The analyses for determining the metals present in the aliquot were performed on an atomic absorption spectrometer Analytik Jena flame spray NovAA400. Table 1 represents the parameters used for the determination of metals. For calibrations and metal determinations, the appropriate synthetic standard (atomic absorption spectroscopy (AAS) multielement standard solution, Merck, Darmstadt, Germany) was employed.

Table 1. Parameters used for the determination of ionic metals in the atomic absorption spectrometer.

Elements	Fe	Mn	Ca	Mg
Lamp current	7.5 mA	10 mA	6.5 mA	6.5 mA
Flame	Air/acetileno	Air/acetileno	Air/acetileno	Air/acetileno
Spectral resolution	0.8 nm	1.2 nm	1.2 nm	1.2 nm
Wavelength	248.3 nm	279.8 nm	422.7 nm	202.6 nm
Combined gas flow	55 L h ^{−1}	55 L h ^{−1}	55 L h ^{−1}	55 L h ^{−1}
concentration unit	mg L ^{−1}	mg L ^{−1}	mg L ^{−1}	mg L ^{−1}

3. Results

3.1. NC Preparation and Interaction with Metals

The NC was obtained by a chemical process referred to as cellulose nanowhiskers. The structure of NC was characterized by scanning electron microscopy (SEM). SEM observations showed that the original cotton linter was successfully acid-hydrolyzed into cellulose nanowhiskers and/or nanocrystalline cellulose with a needle- or short rod-like structure and an average diameter of 15 nm (Figure 2). The fibers have a very wide size distribution, as is often observed for cellulose nanocrystalline structures [15–18]. The NC presented particle agglomeration and consequent stacking, mainly due to its very small size and its large surface area. Furthermore, the hydroxyl group of the surface of the nanowhisker facilitates hydrogen bond formation, which itself facilitates the aggregation.

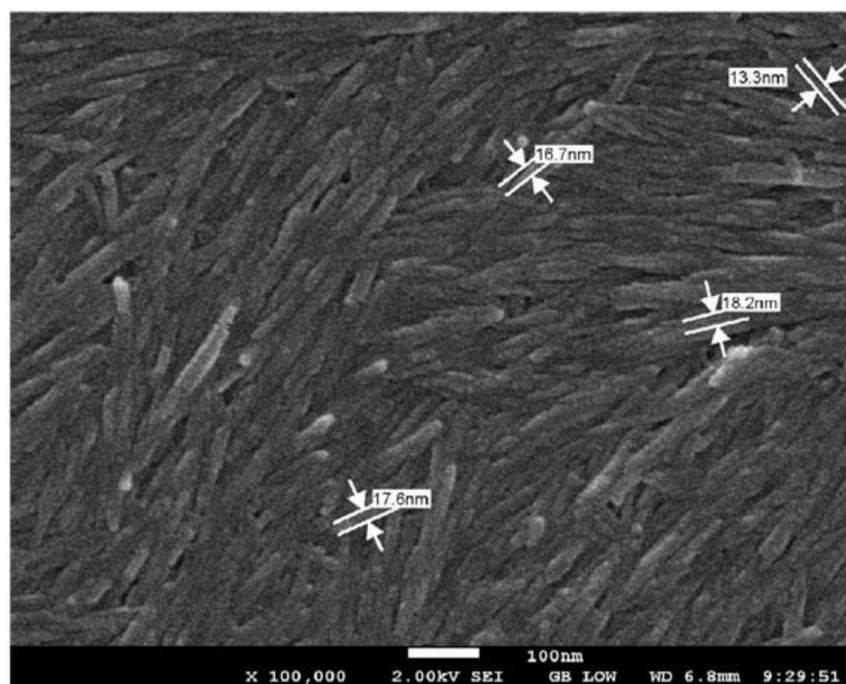


Figure 2. Characterization of cotton linter NC by scanning electron microscopy (SEM).

Figure 3 shows the interaction of nanocellulose with approximately 2 mg L^{-1} of Fe and Mn ions as a function of the volume of NC suspension. Fe has a greater ability to complex with NCs than Mn. Most of the Fe ions were already complexed with the addition of $50 \text{ }\mu\text{L}$ of NC suspension, and the increase in concentration did not lead to significant variations. As regards the Mn with the addition of $100 \text{ }\mu\text{L}$ of NC suspension, a level of complexed metal was already obtained, which remained constant even with the addition of larger volumes of NC.

This confirms that the interactions between Mn and NC do not depend on the amount of NC present in the system. What probably occurs in this system is the arising of labile manganese, where there is the formation of weak bonds that constantly alternate in association and disassociation with the NC. Considering that even with the addition of nanocellulose, free ions remain, the analysis of all metallic ions proceeded with a fixed volume of nanocellulose suspension and the evaluation of the contact time.

In the evaluation of the interaction of NC with Ca and Mg, it was observed that Ca had a low capacity to complex with NC. The proportion of complexed ions varied between 7% and 12% throughout the analyzed period. Compared to results from the literature, it is observed that Ca generally has a lower affinity for humic material than other metallic species [19]. However, it is possible to observe a small Ca—NC interaction (Figure 4). Mg compared to Ca showed a greater complexing capacity in the first 30 min with 28% of the metal forming complexes with the NC. However, after 24 h, the percentage of complexed

Mg dropped to 4%. This behavior indicates that the bonds between NC and Mg can be weak and unstable.

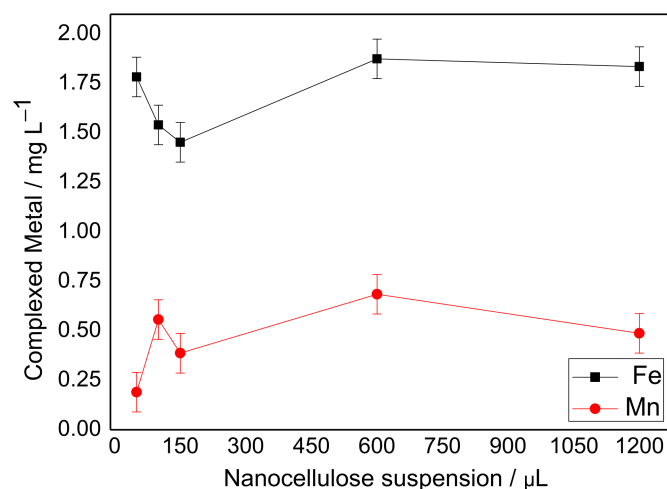
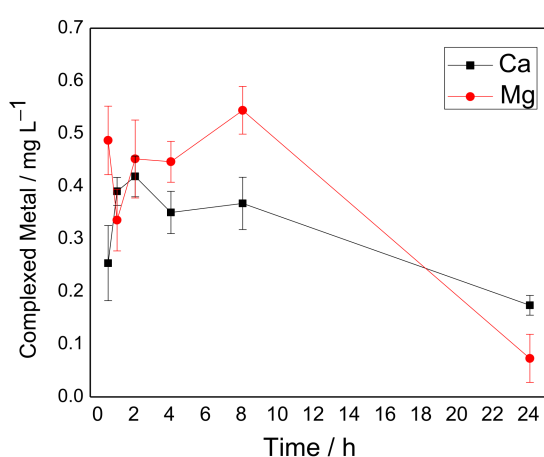
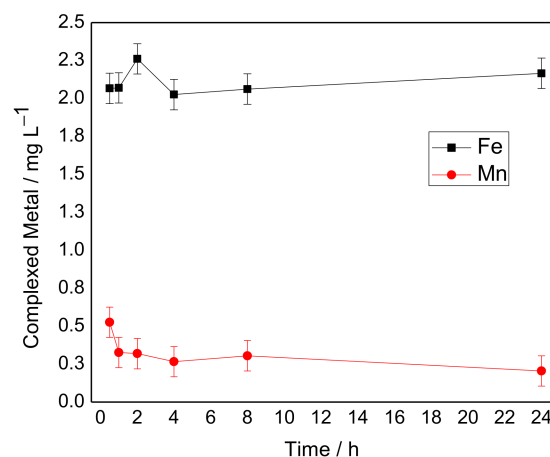


Figure 3. Metals complexed with nanocellulose as a function of the addition of the nanoparticle suspension in the absence of organic matter after 24 h of complexation. pH 5.5. Metal: Fe(II), Mn(II) (2.0 mg L^{-1}). Nanocellulose: 0–1200 μL .



(a)



(b)

Figure 4. Complexed metals to NC in relation to the contact time (a) Metal: Ca(II), Mg(II) (2.0 mg L^{-1}). (b) Metal: Fe(II), Mn(II) (2.0 mg L^{-1}). pH 5.5. Nanocellulose: 300 μL .

When the interaction of Fe with the nanomaterial was evaluated, it was observed that practically all the Fe present in the solution was complexed with the NC, and there were no changes over the analyzed period, indicating that Fe–NC bonds are strong and stable (Figura 4b). Regarding Mn, the graph suggests a low interaction between the metal and the NC, as observed with Ca and Mg. It is likely that weak and unstable bonds form, so there was less complex Mn during the entire period analyzed.

3.2. Influence of NC on Metals–EfOM Complexes

The values for total metal, free metal (filtrate) and complexed metal (difference between total metal and free metal) with the addition of only EfOM without NC are shown below. The fractionation in tangential flow indicated that 44% of Ca ions, 53% of Mg ions, 75% of Fe ions and 88% of Mn ions were complexed with EfOM (Table 2). These results were obtained before the addition of NC to the system.

Table 2. Fractionation of metal ions complexed to EfOM before adding NC to the system.

	Concentration of Metals (mg L ⁻¹)		
	Total Metal $\pm \sigma$ (M + M—EfOM)	Free Metal $\pm \sigma$ (M)	Comp. Metal $\pm \sigma$ (M—EfOM)
Ca	2.199 \pm 0.074	1.229 \pm 0.061	0.971 \pm 0.134
Mg	2.284 \pm 0.010	0.987 \pm 0.036	1.212 \pm 0.238
Fe	2.231 \pm 0.153	0.569 \pm 0.017	1.662 \pm 0.170
Mn	2.228 \pm 0.044	0.269 \pm 0.029	1.959 \pm 0.073

With the addition of NCs to the system, competition between ligands occurs. Complexed metal is represented as M—NC and/or M—EfOM. The influence of the addition of NC to the metal—EfOM complex indicated that iron ions are still complexed, probably to EfOM. Depending on the time of concentration of the complexed Ca, the Mg and Mn decreased, indicating that the metal was supplied in a solution (Figure 5a).

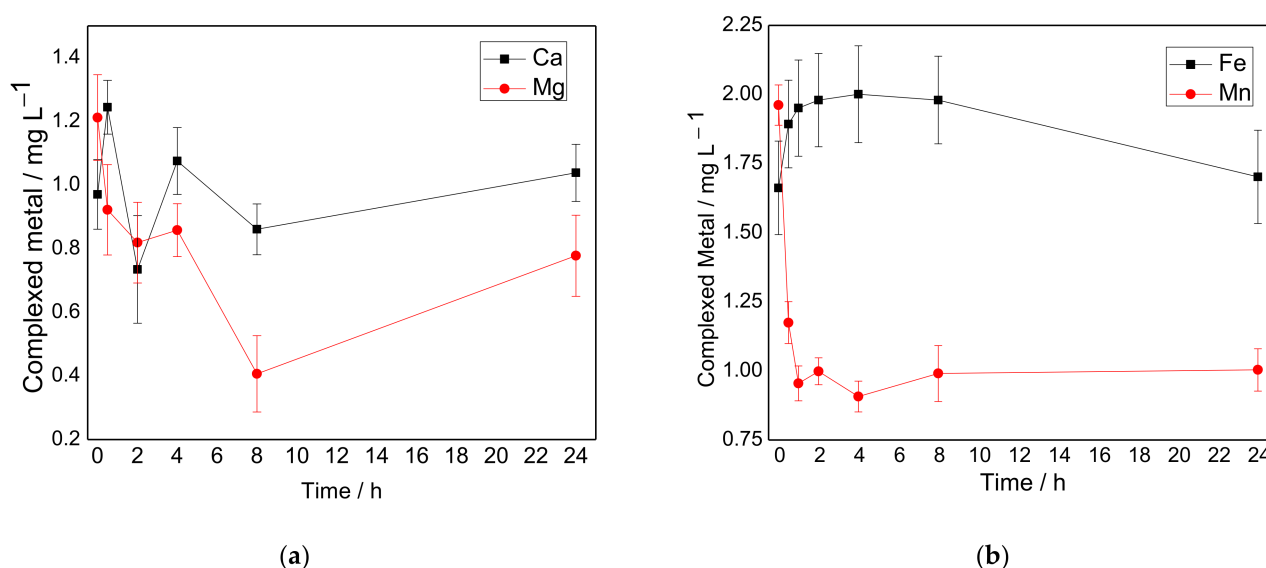


Figure 5. Analysis of the influence of NC on M—EfOM complexes (metals—effluent organic matter). (a) Metal: Ca(II), Mg(II) (2.0 mg L⁻¹). (b) Metal: Fe(II), Mn(II) (2.0 mg L⁻¹). pH 5.5. EfOM: humic substances (100 mg L⁻¹). Nanocellulose addition: 300 µL.

For Ca, only 44% of the ions complexed with EfOM before the addition of the NC; after 30 min of the addition this value increases to 57%. However, the next points indicate a very large variation in relation to the number of complexed Ca ions. As previously noted, NC forms weak bonds with Ca and tends to release the labile metal into the system, so Ca is sometimes linked with NC, and sometimes it is free, which explains the variation. In addition, the points at which the number of complexed Ca is less than $t = 0$ may suggest that part of the complexed metal, EfOM, migrates to the NC, which then tends to release the metal due to the low quality of the interaction. Regarding Mg ions, 53% complexed with EfOM, and after the addition, all points indicate a decrease in the number of complexed ions, so the metal may have migrated from EfOM to NC, just as occurred with Ca.

After the addition of NC to the system, there was a small increase in the amount of Fe complexed in the system, which may indicate that part of the metal that was free at time zero was complexed with the NC. However, Fe has the ability to form strong bonds with the two ligands, so it is plausible that there has been an increase in the number of complexed ions. After the addition of NC to the Mn—EfOM complexes, there was a reduction in the complexed Mn ions. This may have happened due to the competition between NC and

EfOM. In this system, the complex of Mn and EfOM migrates to the NC, and ends up forming weaker interactions, releasing the metal more easily (Figure 5b).

3.3. Influence of Organic Matter on M—NC Complexes

The values for total metal, free metal (filtrate) and complexed metal (difference between total metal and free metal) with only NC addition and without organic matter are shown in Table 3. It is observed that, except for Fe, the metals evaluated showed low complexation with NC.

Table 3. Fractionation of metal ions complexed to NC before adding EFOM to the system.

	Concentration of Metals (mg L ⁻¹)		
	Total Metal $\pm \sigma$ (M + M—NC)	Free Metal $\pm \sigma$ (M)	Comp. Metal $\pm \sigma$ (M—NC)
Ca	3.400 \pm 0.018	3.290 \pm 0.017	0.109 \pm 0.035
Mg	1.720 \pm 0.035	1.647 \pm 0.011	0.073 \pm 0.046
Fe	2.468 \pm 0.013	0.196 \pm 0.011	2.272 \pm 0.024
Mn	2.236 \pm 0.202	2.107 \pm 0.036	0.129 \pm 0.238

Figure 6 represents the influence of EfOM on the M—NC complexes. In this case, the first point on the graph (0 h) corresponds to the moment before the addition of EfOM to the M—NC complex.

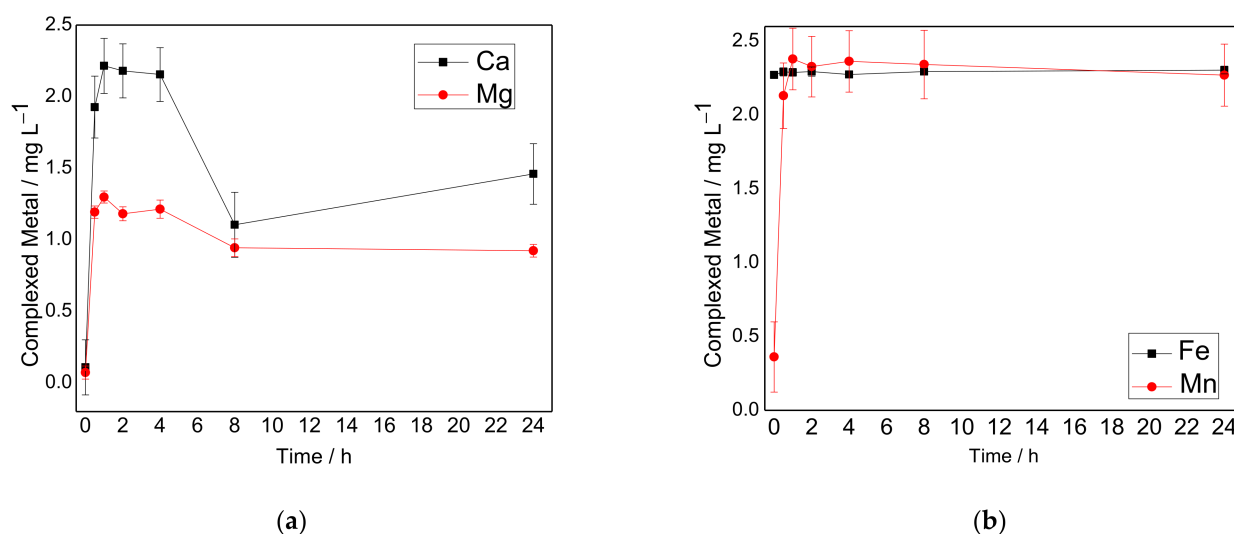


Figure 6. Analysis of the influence of EfOM on M—NC complexes (metal—nanocellulose). (a) Metal: Ca(II), Mg(II) (2.0 mg L⁻¹). (b) Metal: Fe(II), Mn(II) (2.0 mg L⁻¹). pH 5.5. Nanocellulose: 300 µL. EfOM addition: humic substances (100 mg L⁻¹).

For Ca, the addition of EfOM into the system caused a large increase in the portion of complexed ions, which went from 3% to 57% 30 min after the addition of EfOM into the system. The next points indicate stability, but 8 h after the addition there was a decrease in the portion of complexed ions. The EfOM was shown to have a greater capacity to complex Ca compared to NC; however, the presence of the two ligands in the system can cause a competition scenario, where Ca passes to the NC forming less stable complexes. The Mg initially presented a behavior very similar to the Ca—before the addition of EfOM into the system, only 4% of the Mg had formed complexes with the NC, and after 30 min from the addition of EfOM into the system, the portion of complexed ions rose to 69%; after 480 min, a slight drop in the number of complexed ions was observed, which rose to 55%, and at the

end of 24 h, the portion increased to 54%. The same considerations were made as for Ca, the fall can be justified by a competition between EfOM and NC.

For Fe, the addition of EfOM did not change the proportion of the complexed metal to NC; this is because Fe was shown to be able to form strong bonds with both NC and EfOM (Figure 6b). As for Mn, it can be observed that the proportion of the metal bound to NC was very low before the addition of organic matter (time 0 h); however, after the addition of EfOM, practically all Mn was complexed, and there were practically no changes in this time. This may have happened because, in a competitive scenario among binders, EfOM stands out by forming stronger bonds with Mn.

4. Discussion

The absorbance values found in UV-VIS spectrophotometry at wavelengths of 465 and 665 nm by Vieira et al. [20] indicate that HS does not present such a high degree of structural condensation, which explains the interaction between metal and EfOM.

The competition scenario may cause an increase in the bioavailability of metals due to their weaker bonds with NC. In addition, the competitive elements can also collaborate, so that the metal—NC bonds are absorbed by living beings due to the reduced size of the nanomaterial.

There is probably an interaction between EfOM and nanocellulose. In the first case, where the M—EfOM complexes are in equilibrium, upon coming into contact with the nanomaterial, manganese is released into the environment. In addition, its removal from the effluent is ineffective, increasing its toxicity and impact on the environment, due to its availability in the free metal format.

In the second case, where the M and NC are in equilibrium, when exposed to organic matter, the complexed ions increase. As regards the effluent treatment, the organic matter carrying the ion would probably be incorporated into the NC carrying the metallic ion, overloading the complexation capacity of the NC and blocking the interaction of M with NC.

In the case of Fe, removal is effective even in the presence of organic matter, this being an interesting option for iron removal in effluents containing organic matter, such as wastewater treatment plants. Regarding Ca, Mg and Mn ions, it is possible to verify that there was competition between the complexing groups present in the EfOM and the NC releasing the metal into the solution (free metal). To increase the NC—metal interaction, it could be interesting to develop an organomodification process through the incorporation of selective groups on the surface of the nanomaterial.

Several studies have reported the use of nanocellulose in emerging applications, and focused on the characteristics of this material, such as its high surface area to volume ratio, low environmental impact (mainly for not having associated metals that can be released into the environment), high strength, functionalization and sustainability, and its ability to be applied as a film on support surfaces in the remediation of aquatic environments.

5. Conclusions

This work proposes the valorization of an agroindustrial residue, a fibrous cotton residue, in a nanotechnological input, to be applied in several segments of the technology industry. The results presented in this study show that NC causes changes in the complexation mechanism of metals mixed with organic matter present in water (EfOM). Fe ions showed strong interactions with NC. In relation to Ca, Mg and Mn ions, it is possible to verify that there was competition between EfOM and NC, such that the metal is free in the solution. To increase the NC—metal interaction, it may be interesting to develop an organomodification process, through the incorporation of selective groups onto the surface of the nanomaterial. Nanocellulose has showed high potential for use in the development of new technologies for the treatment of effluents containing metals, mainly iron.

Author Contributions: Conceptualization, J.C.C.; methodology, D.G.; investigation, V.d.J.C.d.S.; data curation, V.d.J.C.d.S.; writing—original draft preparation, V.d.J.C.d.S.; writing—review and editing,

W.G.B. and L.C.d.O.; project administration, D.G.; funding acquisition, D.G. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by São Paulo Research Foundation (FAPESP), #2019/24684-2 and #2018/21747-0.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The study did not report any data.

Acknowledgments: Vicunha Rayon Ltd. a for the donation of cellulosic cotton linter fibers.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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