Remediation of contaminated water with Chromium VI by sorption in surface-activated-nanocellulose

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Research Article

Keywords: Cr VI, nanocelullose, pH, sorption, Freundlich and Langmuir isotherms

Posted Date: April 19th, 2021

DOI: https://doi.org/10.21203/rs.3.rs-334803/v1

Abstract

Chromium VI is a frequent pollutant of industrial liquid effluents resulting from industrial waste. It is a substance classified into the carcinogen group I. In this study, a Cr VI sorption mechanism was developed by using nanocellulose beads (hydrogel) obtained from ivory nut. Cr VI was detected in water by a colorimetric method, using 1, 5-diphenylcarbazide at λ 540 nm. The sorption capacity of nanocellulose spheres was tested by varying the solution's pH and temperatures. Our results showed that nanocellulose can efficiently adsorb at pH 4 and 25°C. Removal percentages were between 91.29%(+/-1.36) and 95.33% (+/- 0.86) of the total Cr VI. The sorption kinetics showed that the material reaches equilibrium after 20–30 minutes. Additionally, an analysis of adsorption isotherms showed a high fit with the Langmuir and Freundlinch isotherms. Therefore, this method seem to be applied both to decontaminate industrial and drinking water employing an organic matrix such as nanocelullose beads.

Article Highlights

The research conceives and develops a new sorption material based upon ivory nut nanocellulose beads. The results showed the material's capacity as an adsorption agent, capable of efficiently capturing Cr VI. The proposed method for capturing Cr VI through nanocellulose hydrogels beads proved to be an appropriate strategy to remediate water. It was possible to recover remediated water while nanocellulose beads were able to embed the contaminating agent. The ability of the embedding material was tested at different pH and temperatures. Finally, results are shown in the data analysis.

1 Introduction

Water pollution is one of the most significant challenges facing humanity (Kardam et al. 2014), As water is a natural resource on which social, economic, and ecosystem activities depend (Westall and Brack. 2018). Water pollutants can be organic such as hydrocarbons, esters, pesticides, aromatic compounds (Wilson and Jones. 1993); or inorganic, such as heavy metals (Chowdhury et al. 2016).

One of the primary sources of water contamination is heavy metals, which can be introduced into the environment naturally due to volcanic activity (Park et al. 2000), rock erosion and forest fires, or anthropogenic activities such as mining, agriculture, and industry (Owa. 2013). Metals such as Cu, Zn, Ni, Pb, Cd, and Cr have been found to harm human and animal health (Adimalla. 2020). Chromium is one of the metals of most significant interest since it is widely used to preserve wood, prepare chromates, and produce plastic and pigments, among others (Oladoja et al. 2013). Cr VI resulting from industrial waste contaminates countless bodies of water worldwide (Kardam et al. 2014). Besides, the International Agency for Research on Cancer has classified this element in carcinogen group I (Straif et al. 2009); because several studies have shown that it can cause lung and gastrointestinal tract cancer (Zhang et al. 2020).

There are multiple techniques to improve water quality when it is contaminated with Cr VI. Some of those are oxidation-reduction (Li et al. 2017); phytoremediation (Rezania et al. 2015); ion exchange (Fu and Wang; 2011); precipitation (Cainglet et al. 2020); capture by biopolymers (Gupta and Diwan. 2017); adsorption (Fu and Wang. 2011); membrane filtration (Owlad et al. 2009); biosorption (Abdolali et al. 2017); and capture by nanoparticles (Qu, Alvarez, and Li. 2013). Furthermore, among the most promising techniques are those that use nanoparticles to remove Cr VI from water (Bhattacharya et al. 2013); nanoparticles measure less than 100 nm in at least one of their three dimensions (Klemm et al. 2018). The advantage of using them is the large surface area they present; many contain high reactivity and sorption capacity (Klemm et al. 2018).

Nanosorbents, such as modified membranes, nanophytocatalytic particles, and magnetic nanoparticles, are the most common sorption agents (Qu et al. 2013);biomass is one of the most common sources for obtaining nanosorbents due to the comparative advantages over other sorbents (Singh et al. 2020). This advantages includes low cost, high efficiency, regeneration capacity, and high availability (Dorishetty et al. 2020).

Besides, Nanocellulose fibershas properties that stand out for many applicationsits extraction from lignocellulosic biomass, especially from agricultural residues, has been extensively studied (Tshikovhi et al. 2020); in those cases, non-cellulosic materials such as lignin and hemicellulose are removed by a pretreatment (Phanthong et al. 2018). The separation of lignin and other molecules combined with cellulose in lignocellulosic materials requires intensive energy input and, frequently, the use of polluting chemicals (Portero et al. 2020).

NC retains several cellulose properties, such as its hydrophobicity, crystallinity, and ability to be modified (Klemm et al. 2018). Three types of these particles can be found: nanocellulose crystals (CNC), cellulose nanofibrils (CNF), and bacterial nano cellulose (BNC). They differ from each other in their origin and in the obtainment methods, functionalization, shape, particle size, size dispersity, and mechanical characteristics (De France et al. 2017).

In this framework, the use of non-lignocellulosic feedstocks may facilitate NC's extraction (Haafiz et al. 2013). To illustrate, in the western forests of Ecuador, there are palms of the species *Phytelephas aequatorialis*. Its seeds (tagua) are used mainly to make buttons for the fashion industry (Montufar, 2013). This process produces about65-88% of tagua waste, which currently represents about 4,800 t / year (Valencia et al, 2013). In this research, it has been demonstratedthat high purity nanocellulose can be obtained from the endosperm of *Phytelephas aequatorialis* seeds.. This material is suitable for metal sorption (Mautner et al. 2019).

Moreover, NC has been widely used for its mechanical and chemical properties. The hydroxyl groups present on its surface allow a relatively easy chemical modification (Oun et al. 2019). The modifications lead to an increase in the range of applications of these nanoparticles. Besides, the most critical modification employed for metals or their metallic salts capture on NC, is the esterification with positive

or negative groups to the primary and secondary hydroxyl groups of glucose (Gan et al. 2020). Modified NC can bind charged molecules via ionic linkages.

This study reports the use of tagua NC beads for the remediation of Cr VI contaminated water. Through the use of specially tailored hydrogel beads masked with quaternary ammonium. It is proved to be an up-and-coming technique insofar as it has been possible to remove up to between 91.29–95.33% of Cr VI in an aqueous solution.

2 Materials And Methods

2.1 Acid extraction of nanocellulose.

The nanocellulose fibers were prepared through hydrolysis using sulfuric acid. Then, 20 g of tagua pulp was chopped in a blender. Next, 175 mL of sulfuric acid was added at a concentration of 64% w/w preheated to 45 ° C. The reaction continued for 60 minutes at 45 ° C. Subsequently, the solution was dissolved at 10% of the initial Concentration to stop the reaction. Finally, it was centrifuged and washed using dialysis membranes until the pH was neutral (Menon et al. 2017).

2.2 Atomic force microscopy of the obtained material (AFM)

The shape and approximate size of the NC particles were measured by using a Brucker — model dimension icon AFM. This allowed to characterize nanoparticles in width, depth, and length. A series of dilution factors were tested to obtain individual fiber nanoparticles. The most appropriate was the dilution of 2×10^{-3}.

2.3 Nanocellulose hydrogel spherification

A solution was prepared with 1.46 g of quaternary ammonium in one liter of water (Bingol et al. 2004). The sol-to-gel transition of the aqueous solution of nanocellulose (1% w/v), was attained by dripping 10 mL of nanocellulose onto 25 mL of a quaternary ammonium solution preheated at different temperatures (50, 60, 70 and 80 ° C).

2.4 Colorimetric method for detection of Cr VI

First, 1.5 g of 1,5-diphenylcarbazide (complexing agent) were dissolved in 50 mL of acetone (Huang et al. 2020).Then, a mix of 10 µL of H_2SO_4 50% v/v solution, and 20 µL of the complexing agent were dissolved in 1 mL of a solution with $K_2Cr_2O_7$. Finally, a spectrophotometer (Helyos β, Thermospectronic) was used to detect the presence of Cr VI at 540 nm (Mohamad et al. 2013).

2.5 Preparation of Cr (VI) solutions and calibration curve tailoring

A stock solution (1,000 mg Cr(VI)/L) was prepared by dissolving 2.829 g of $K_2Cr_2O_7$ (CAS 7778-50-9; ≥99.0%; Sigma–Aldrich) in 1 L of deionized distilled water.For nanocellulose beads sorption experiments,

diluted solutions were prepared with concentrations ranging from 10 to 100 mg Cr(VI)/L (Campaña, 2019). Subsequently, a calibration curve type was tailored by using concentrations within the range 0.01 to 1 mg/L, to obtain a linear equation. This equation was used to calculate the Concentration of Cr VI in water.

2.6 Influence of pH and temperature in nanocellulose sorption of Cr VI

A series of Cr VI solutions of 10 and 100 mg/L were adjusted at pH 4, 6 and, 8, respectively. The solutions were tested at temperatures of 15, 20, and 25 (° C). Nanocellulose beads were added to each Cr VI solution in a ratio of 1:2. Then, they were stirred for 3 hours at the temperatures mentioned above. The experiments were performed by triplicate.

2.7 Metal removal calculation

The Concentration of the solution exposed to the NC spheres was calculated. The percentage of metal removal (% MR) was obtained with equation 1:

$$\% RM = \frac{Ci - Ce}{Ci} * 100 \qquad (1)$$

Where: *Ci* is the initial Concentration, and *Ce* is the final Concentration of Cr VI (Zhu et al. 2014

2.8 Statistical analysis.

An angular transformation was made on the % MR in order to normalize the data expressed in terms of percentage for statistical analysis. Consequently, ANOVA calculated the significance, and a Tukey test was established to determine the optimal Cr VI sorption conditions (Lee & Lee, 2018).

2.9 Cr VI adsorption kinetics

Once optimum pH and temperature were established, a series of solutions of Cr VI at concentrations 10, 25, 50, 75, 100 (mg/L), were added to nanocellulose gel beads at a 2:1 volume rate. The tests were carried out by triplicate at 10, 15, 20, 30, 90, 120, and 180 minutes.

Subsequently, the % MR and the Concentration of Cr VI removed were plotted as a function of time. Finally, the Concentration of metal adsorbed on nanocellulose beads was evaluated with equation 2:

$$q_e = (c_i - c_e) * \frac{v}{w} \qquad (2)$$

Where: q_e is the amount of metal adsorbed at equilibrium (mg/g); c_i is the initial and equilibrium Concentration (mg/L); c_e is the equilibrium concentration (mg/L); v is the volume of solution (L); and w is the amount of biosorbent (g) (Zhu et al., 2014).

2.10 Analysis of adsorption isotherms:

Two isotherms were evaluated, the Langmuir's and Freundlich's isotherms. Equations 3 and 4 were used for this purpose:

$$q_e = \frac{q_m * b * c_e}{1 + b * c_e} \quad (3)$$

$$q_e = k_f * c_e^{\frac{1}{n_f}} \quad (4)$$

Where q_e is the amount of metal adsorbed in equilibrium (mg/g); q_m is the maximum amount of adsorbate adsorbed (mg/g); c_e is the final Concentration of the metal (mg/L); b is the Langmuir constant (L/mg); n_f is the affinity constant between adsorbate and adsorbent; and k_f is the Freundlich constant (Yao et al. 2016).

2. 11 Column filtration of contaminated water with Cr VI

A column of 26 cm long, 1 cm diameter and 20 mL capacity was packed with NC beads. Then it was filled with Cr VI solutions. After that, the samples were injected under pressure. Finally, the experiments were carried out with Cr VI solution concentrations of 10, 100 mg/L, 25°C, for 20 and 30 minutes.

3 Results And Discussion

3.1 Acid extraction of nanocellulose.

According to Meier (1958); from the acid extraction of nanocellulose, 65% of the cellulose contained in the tagua seed can be recovered. What's more,nanocellulose presents *in situ* gelation due to ionic linkages. Those are lead by metal ions with negative charges esterified to OH groups in nanocellulose (SO_3^-).

So, this feature allows the formation of nanocellulose gel beads. In fact, the porosity of the beads is related to the nanocellulose concentration in the cellulose/water suspension.

3.2 Atomic force microscopy (AFM) of nanocellulose fibrils

Before gelation, the extracted nanocellulose presents a massive ultrastructure. Where single bundles or fibrils are almost impossible to distinguish.

After ultrasonic disruption of cellulose bundles, nanofibrils get separated by thin H_2O layers. The individual fibrils are visible after a series of dilutions with water (**Fig 1**). Also, the elongated fibrils vary in terms of dimensions within a range of 3-5nm in width. Remarkably, these fibers present longitudinal

folding that generates angles. Thus, this characteristic contributes to the entanglement of gels (Chaabouni & Boufi, 2017).

3.3 Nanocellulose Spherification

The optimum formation of gel beads (in terms of its consistency and shape) was attained at 70°C. The spheres were formed with an average diameter of 2 mm. Besides, heat enhances the interaction between cationic surfactants and negative charges of nanocellulose. Consequently, the resultant beads' consistency and shape are obtained through the functional groups' interaction (Bora and Dutta. 2014).

As far, the nanocellulose produced for this work was obtained from the fractionation of the endosperm of tagua (*Phytelephas aequatorialis*). It is an acid-hydrolyzed treatment with sulfuric acid. As a product it acquires a surface charge, given by the esterification of OH groups in glucose with SO_3^- groups. According to previous analyzes (unpublished data), it is known that this nanocellulose contains 0.128 mmol- SO_3^- / g. As well,the concentration of SO_3^- groups esterified to OH groups in glucose, depends on the process's acid hydrolysis conditions. For instance, Harris & McNeil (2020) found 0 - 1.9 mmol SO_3^- / g.

On the other hand, quaternary ammonium is a cationic surfactant that has been used on clays and zeolites since it improves the affinity with non-ionic and hydrophobic organic compounds (Li & Bowman. 1998). It has also been used to modify the surface of nanocellulose (He et al. 2014). For example; Li et al. (2018) used quaternary ammonium to promote antibacterial activity in nanocellulose-based materials (Chen et al. (2017) used ammonium-modified nanocellulose to degrade methyl orange dye.

Moreover, quaternary ammonium is a cation with an NR_4^+; where R represents the alkyl/aryl group structure (Gerba. 2015) that can easily interact with the SO_3^- functional group of nanocellulose fibrils. When nanocellulose was dripped on dissolved quaternary ammonium, crosslinking occurred with additional surface charge change. This charged surface interacts with Cr VI in aqueous solution (Li et al. 2018).

3.4 Cr VI sorption based on pH and temperature

The ANOVA did not show statistically significant differences for the temperature treatments. The pH is the only factor that affects the % MR significantly. Additionally, Tukey's test showed the higher Cr VI removal at pH 4.0.

In several studies, the influence of pH for the sorption of Cr VI was evaluated. These have shown that this factor (pH) has a significant impact on the percentage of removal (Tovar et al, 2014). It is also known that Cr VI can be present in many forms such as H_2CrO_4, $HCrO_4^-$, CrO_3^{-2} and $Cr_2O_7^{-2}$;depending on pH and its Concentration (Jiang et al, 2014). Thus, when the pH is between 1 and 4, the predominant form is $HCrO_4$. It interacts with the monovalent anion NR_4^+. Next, when the pH increases, the most common

forms of Cr VI are $Cr_2O_7^{-2}$ and $Cr_2O_4^{-2}$. So that two anions of NR_4^+ interact with those forms of Cr VI. Consequently, with a higher pH the MR % decreases (Karthikeyan et al, 2005).

The results of this research coincide with those obtained in a study carried out by He et al. (2014) which reported that the highest Cr VI sorption values were between pH 3 to 4. Moreover, an acidic pH is favorable because of protons' (H^+) increase on the nanocellulose surface. Giving rise to a strong electrostatic attraction between the positively charged surface and the chromate ions (Fijałkowska et al. 2020).

According to the ANOVA results, the temperature variation in the experiments did not show a statistical significance. Nevertheless, a slight enhancement of Cr VI sorption at higher temperatures would be associated with the reaction's endothermic nature. This phenomenon can be explained by the increase of the intraparticular diffusion rate of Cr VI ions, into the nanocellulose beads' pores (Zhang et al. 2014).

3.5 Adsorption kinetics

The final Concentration of Cr VI decreases until the matrix is saturated. In Table 1, it can be observed that the Concentration decreases progressively until it reaches 20 to 30 minutes.

Since the % MR increased as time passed; all the samples were exposed for 180 min (3 h). However, it can be seen that the majority of the samples reached their maximum % MR much earlier (Table 2). While in the study done by He et al. (2014) it took around 50 minutes to obtain an efficiency of almost 100%. In the research of Jiang et al (2014), sorption equilibrium was obtained at 120 min. This because HA-Fe_3O_4 was used to adsorb Cr VI; resulting in a % MR of 80 to 90%. On the other hand, Zhu et al. (2014) studie's obtained a 80% efficiency in 10 minutes.

3.6 Analysis of adsorption isotherms

Water remediation must include an isotherm analysis to determine its effectiveness (Lombardo and Thielemans 2019). Additionally, it is essential to establish an equal saturation time to increase its productivity.

Two adsorption isotherms were evaluated: Langmuir's and Freundlich's. For the Langmuir isotherm, a linear graph was constructed as a function of the final metal concentration (mg/L) (*ce*); and the amount of metal adsorbed at equilibrium (mg/g) (*qe*). As a result, an R^2 of 0.979 was obtained out of the linear regression.

For the Freundlich isotherm, another linear regression was obtained, whose R^2 was 0.966. In addition, the values of the heterogeneity factor (*n*) were calculated. As well as the Freundlich constant (k_f) which is associated with the adsorption capacity. The values obtained were 0.8917 and 1.31025 $[(mg / g)^{-1}/n]$ respectively.

The results obtained were adjusted to Langmuir's isotherm, meaning that the surface of the adsorbent and all the sorption sites are homogeneously distributed. Besides, each cation can interact with a single molecule of Cr VI, forming a monolayer as a consequence (Giles et al.1974). However, results also show a high adjustment to the Freundlich isotherm, which means that multilayer adsorption also occurs (Yao, 2016).

The adsorption method showed very high efficiency compared to other published works. A comparison is shown in Table 3.

3.6 Column filtration

In practical terms, the water treatments are performed in columns that save space; improve the surface contact with the water pollutants; and allows cleaning and or replacement of the adsorbent matrix (Leupin et al, 2005).

The present research, performed adsorption experiments in columns (data not shown). Which had a very similar result when compared to the experiments in beakers. Columns ensure the distribution of the contaminated bed homogeneously in the adsorbent (Ali. 2014). A notable advantage of columns is that the NC matrix can undergo a desorption process after saturation. So they can be reutilized (Figueira et al. 2004).

4 Conclusions

To summarise, the use of a nanocellulose hydrogel as a biosorbent to remedate water contaminated with Cr VI was shown to be an efficient method (% removal of the metal between 91.29–95.33%). The pH produced an increase in the sorption capacity of this material. On the other hand, in the sorption kinetics, a sorption equilibrium was obtained at 20–30 min. Which depends on the metal's initial Concentration.

This experiment fitted the Langmuir adsorption isotherm better than the Freundlich isotherm. High affinity was obtained between the adsorbent and the adsorbate. Also, a high sorption capacity compared to other adsorbents used in similar research.

Finally, the column's use to capture Cr VI showed an efficiency similar to the tests carried out previously. Therefore, nanocellulose beads masked with quaternary ammonium (a porous hydrogel matrix masked by a strong cation) represent a suitable combination to remediate water contaminated with Cr VI. Lastly, nanocellulose beads can also be reutilized after regeneration cycles.

Declarations

Funding: This study was supported by the Pontificia Universidad Católica del Ecuador.

Conflicts of interest: The authors declare there is no conflicts of interest in this study.

Authors' contributions:

Renata Ossa Paredes and Enrique Javier Carvajal Barriga contributed to the conception and design of the study. Renata Ossa Paredes performed material preparation, data collection, and analysis. Patricia Portero Barahona and Bernardo Bastidas supported with experiments set up and data acquisition. The first draft of the manuscript was written by Renata Michelle Ossa Paredes and Enrique Javier Carvajal Barriga. Project writing and funds acquisition was in charge of Enrique Javier Carvajal Barriga. All authors read and approved the final manuscript.

Data availability statement: The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

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Tables

Table 1. Variation on the final Concentration of solutions of Cr VI after being exposed to the sorption matrix during different timeslots.

Time (min)	Initial Concentration mg/L				
0	*10*	*25*	*50*	*75*	*100*
10	2.04 ± 0.03*	4.27 ± 0.38	43.09 ± 0.95	44.60 ± 0.92	27.71 ± 0.96
15	1,22 ± 0.06	2.83 ± 0.19	6.91 ± 0.67	7.37 ± 0.68	26.51 ± 1.21
20	0,68 ± 0.02	2.17 ± 0.20	6.59 ± 0.96	6.21 ± 0.43	10.93 ± 1.04
30	0,69 ± 0.001	2.17 ± 0.34	2.96 ± 0.35	3.49 ± 0.64	8.15 ± 0.66

* Standard deviation

Table 2. Variation of% RM in solutions of Cr VI after being exposed to the sorption matrix for different timeslots.

Time (min)	***Initial Concentration mg/L***				
0	10	25	50	75	100
10	79.34 ± 0.96 *	82.91 ± 1.53	13.81 ± 1.91	40.53 ± 1.23	72.28 ± 0.96
15	87.66 ± 1.216	88.67 ± 0.78	86.17 ± 1.35	90.17 ± 0.91	73.48 ± 1.21
20	93.18 ± 1.04	91.29 ± 0.80	86.81 ± 1.92	91,71 ± 0.58	89.06 ± 1.04
30	93.08 ± 0.66	91.29 ± 1.36	94.07 ± 0.7	95.33 ± 0.86	91.84 ± 0.66

* Standard deviation

Table 3. Different adsorption isotherms reported in the literature

Methodology	*Qm*	b	*n*	Reference
Surface-activated-nanocellulose	588.235	4.25×10^{-5}	0.8917	Current work
Quaternary ammonium-functionalized aerogels	17.66	2.24	-	He et al (2014),
Polyaniline impregnated nanocellulose composite	48.92	2.16	-	Jain et al (2017)
Modified cellulose	22.20	0.214	-	Kalidhasan. et al (2012)
Quitosan	153.850	5.978×10^{-3}	0.7353	Baran et al. (2007)
Chitin	70.422	9.670x10-3	1.76603	Baran et al. (2007)
Agave lechuguilla biomass		2.95×10^{-4}	10.22	Romero et al. (2005)
Surfactant–modified serpentine for fluoride	57.33	2.188		Mobarak et al. (2019)

Figures

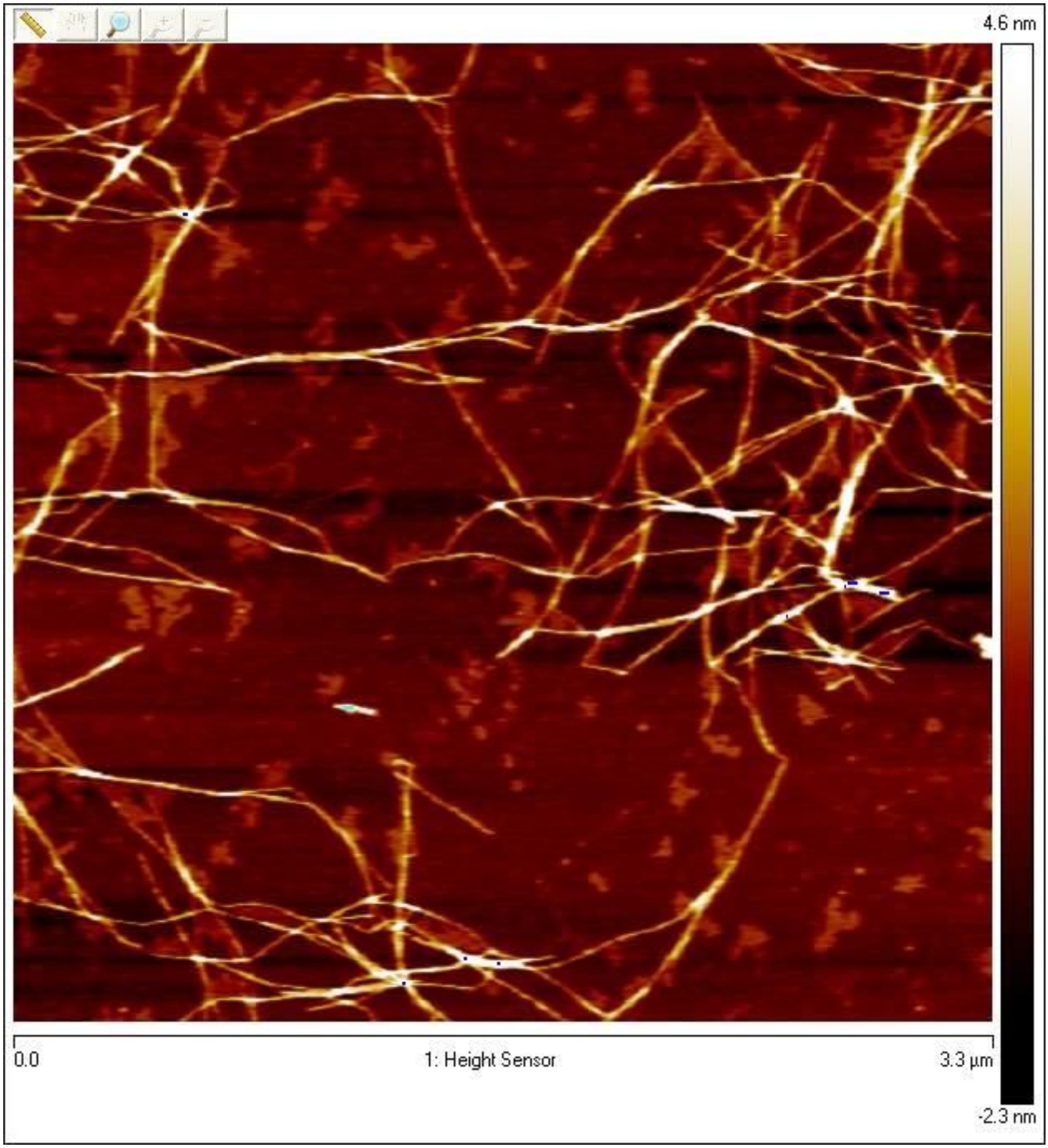

Figure 1

An image of NC fibers in AFM 3.3 um bar scale