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ORIGINAL PAPER

Enhancing adsorption of heavy metal ions onto biobased nanofibers from waste pulp residues for application in wastewater treatment

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Abstract Biobased nanofibers are increasingly considered in purification technologies due to their high mechanical properties, high specific surface area, versatile surface chemistry and natural abundance. In this work, cellulose and chitin nanofibers functionalized with carboxylate entities have been prepared from pulp residue (i.e., a waste product from the pulp and paper production) and crab shells, respectively, by chemically modifying the initial raw materials with the 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) mediated oxidation reaction followed by mechanical

disintegration. A thorough investigation has first been carried out in order to evaluate the copper(II) adsorption capacity of the oxidized nanofibers. UV spectrophotometry, X-ray photoelectron spectroscopy and wavelength dispersive X-rays analysis have been employed as characterization tools for this purpose. Pristine nanofibers presented a relatively low content of negative charges on their surface thus adsorbing a low amount of copper(II). The copper adsorption capacity of the nanofibers was enhanced due to the oxidation treatment since the carboxylate groups introduced on the nanofibers surface constituted negative sites for electrostatic attraction of copper ions (Cu^{2+}). The increase in copper adsorption on the nanofibers correlated both with the pH and carboxylate content and reached maximum values of 135 and 55 mg g^{-1} for highly oxidized cellulose and chitin nanofibers, respectively. Furthermore, the metal ions could be easily removed from the contaminated nanofibers through a washing procedure in acidic water. Finally, the adsorption capacity of oxidized cellulose nanofibers for other metal ions, such as nickel(II), chromium(III) and zinc(II), was also demonstrated. We conclude that TEMPO oxidized biobased nanofibers from waste resources represent an inexpensive and efficient alternative to classical sorbents for heavy metal ions removal from contaminated water.

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Introduction

In the quest for alternatives to oil-based materials, polymers from renewable resources are interesting to consider due to their availability, renewability and reduced environmental footprint. The most abundant natural polymers, cellulose and chitin, are structural elements of plant or animal cell walls, respectively, and are present as stiff microfibrils. Nowadays, these bioresources are considered as excellent candidates for the elaboration of a new generation of biobased materials offering a wide range of properties and functions.

Cellulose and chitin nanofibrils (CNF and ChNF) can be extracted from their source as semicrystalline, long and rather flexible fibrils by a mechanical disintegration process, while crystalline, shorter and stiff rod-like nanocrystals/nanowhiskers are obtained by an acid hydrolysis treatment (Klemm et al. 2011; Siro and Plackett 2010; Habibi et al. 2010). Prior to mechanical disintegration, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO)-mediated oxidation may be pursued to alter the surface chemistry of CNF/ChNF by introducing carboxylates onto their surfaces while maintaining their native crystalline structure (Saito et al. 2007). Negatively charged entities (e.g., carboxylates) in biofiber's surface are attractive in environmental remediation as they can interact with positively charged ions, polyelectrolytes and nanoparticles (O'Connell et al. 2008; Ngah and Hanafiah 2008; Liu et al. 2013).

The small diameter of the nanofibers makes their surface area considerably high. Cellulose nanofibers with a Brunauer–Emmett–Teller (BET) surface area as high as $480 \text{ m}^2 \text{ g}^{-1}$ have been reported (Sehaqui et al. 2011b), and potential applications would be in storage, separation and purification processes. Practical examples are the use of CNF-based aerogels for CO_2 capture from the atmosphere (Gebald et al. 2011) or as air/gas filters (Macfarlane et al. 2012; Fukuzumi et al. 2013). Concerning the use of biobased porous structures for water purification technologies, the possibility to tailor the porosity and pore size of the nanofiber-based membranes (Sehaqui et al. 2010 a, b, Sehaqui 2011; Henriksson et al. 2008; Visanko et al. 2014; Sehaqui et al. 2014) is important for physical separation processes, while the possibility to tune the surface properties of the nanofibers through chemical functionalization strategies can provide additional

separation features through adsorption mechanisms. For instance, heavy metal ions in contaminated water may be removed through adsorption onto nanofiber-based membranes. This requires a systematic study on parameters affecting interactions of metal ions with biobased nanofibers, processing of suitable nanofibers into membrane with well-defined porosity and pore sizes, and finally investigating performance of the membrane for particular application.

Recent studies have used cellulosic nanofibers in membranes for water purification purposes (Sato et al. 2011; Ma et al. 2012a, b). The nanofibers/nanocrystals have been embedded in an electrospun polyacrylonitrile (PAN) nanofibrous scaffold or formed a thin film on top of it, and this package was mechanically supported by a PET non-woven substrate. The multilayered membrane showed interesting results in terms of bacteria and virus removal capability (Sato et al. 2011), radioactive Uranyl (UO_2^{2+}) ions (Ma et al. 2012b) and positive dye adsorption (Ma et al. 2012a).

Copper, Nickel, Chromium and Zinc are heavy metals that occur naturally in rock-forming and ore minerals and are brought to environment through industrial and other domestic processes. Consequently, the contamination of water by these heavy metal ions combined with their toxic effects at high concentration makes it important to find environmentally friendly and cost effective water purification technologies for the removal of these contaminants (O'Connell et al. 2008).

In the present work, oxidized biobased nanofibers were prepared from waste resources using the TEMPO-mediated oxidation approach. The enhancement of heavy metal ions adsorption capacity of the resulting nanofibers due to the surface treatment was then investigated. In the first part of this work, the impact of the nanofibers' surface chemistry onto their copper adsorption is studied at different pHs and thoroughly characterized with UV spectrophotometry, X-ray photoelectron spectroscopy (XPS) and wavelength dispersive X-rays analysis (WDX). Comparison to a reference natural adsorbent used in wastewater treatment, namely a Montmorillonite nanoclay with high cation-exchange capacity is provided. From this successful fundamental study, the second part of this work investigated the adsorption of other heavy metal ions [Ni(II), Zn(II) and Cr(III)] onto highly oxidized nanofibers. Inductively coupled

plasma mass spectrometry (ICP-MS) was employed for this purpose.

Materials and methods

2,2,6,6-Tetramethyl-1-piperidinyloxy free radical (TEMPO), Sodium hypochlorite (NaClO) solution (reagent grade, 10–15 % chlorine) were purchased from VWR international. Chitin powder from crab shell ($M_w \approx 400.000 \text{ g mol}^{-1}$) was purchased from Roth GmbH. Pulp residue, a waste product from pulp and paper industry also called “fiber sludge” (Jonoobi et al. 2012), with a cellulose and hemicellulose content of 95 and 4.75 %, respectively, was kindly provided by Processum AB, Sweden. Note that this pulp residue do not contain polymer additives, sizing chemicals, fillers and biocides. Beech pulp fibers (Arbocel) were kindly provided by J. Rettenmaier & Söhne, Germany. CuSO_4 , CrNO_3 and NiSO_4 with a purity of 99 % were purchased from Sigma Aldrich. ZnCl_2 with a purity of at least 98 % was purchased from Fluka.

Cellulose and chitin nanofibers (CNF and ChNF)

CNF and ChNF were disintegrated as aqueous dispersions of ca. 2 wt% from pulp residue and chitin powder, respectively, by a grinding mechanical treatment using a Supermasscolloider (Masuku Sangyo Co, Japan) (Jonoobi et al. 2012). The grinding was performed until gel formation.

TEMPO oxidised cellulose (TOCNF) and chitin (TOChNF) nanofibers

TOCNF aqueous suspension was prepared from pulp residue according to a previously reported method by Saito et al. (Saito et al. 2007) where the pulp residue slurry was mechanically beaten, then dispersed in water in which sodium bromide and TEMPO were dissolved (1 and 0.1 mmol per gram of pulp residue, respectively). The concentration of the pulp residue in water was 2 wt%. The reaction was performed by addition of sodium hypochlorite dropwise into the suspension while maintaining the pH of the reaction at ca. ten by sodium hydroxide addition. Four different oxidation degrees were achieved by choosing four different amounts of hypochlorite (1, 3, 6 and 10 mmol per gram of pulp residue). After all NaClO

was consumed, the oxidized pulp residue was filtered and washed several times with deionized water until the filtrate solution was neutral. The purified pulp fibers were then dispersed in water at a concentration of ca. 0.5 wt% and disintegrated in a Microfluidizer M-110Y (Microfluidics Ind., USA) to achieve a TOCNF aqueous suspension. Similarly, TOChNF from beech pulp fibers and TEMPO oxidized chitin nanofibers (TOChNF) from chitin powder were prepared according to the same method by using 10 mmol g^{-1} of NaClO.

Scanning electron microscopy

Prior to SEM observation, biobased nanofibers were subjected to supercritical drying as reported elsewhere (Sehaqui et al. 2011b). They were then placed on a specimen holder, sputter-coated directly with a platinum layer of about 7.5 nm (BAL-TEC MED 020 Modular High Vacuum Coating Systems, BAL-TEC AG, Liechtenstein) in Ar as a carrier gas at 0.05 mbar. SEM was carried out using a FEI Nova NanoSEM 230 instrument (FEI, Hillsboro, Oregon, USA). SEM images were recorded with an accelerating voltage of 5 kV and a working distance of 5 mm.

FTIR

Infrared spectra of unmodified CNF and TOCNF films prepared by ambient drying of the suspension were recorded using a FTS 6000 spectrometer (Portmann Instruments AG, Biel-Benken, Switzerland). For each sample, the diamond crystal of an Attenuated Total Reflectance (ATR) accessory was brought into contact with the area to be analyzed. All spectra were recorded between 4,000 and 600 cm^{-1} with a resolution of 4 cm^{-1} and 32 scans. The spectra were normalised with respect to the peak located at 897 cm^{-1} corresponding to the C–O–C stretching vibration at the β -(1 → 4)-glucosidic linkage of cellulose (Nelson and O'Connor 1964).

Elemental analysis

Microelemental analyses of carbon, hydrogen and oxygen on nanofiber films were performed by the microelemental laboratory of ETH-Zurich on a LECO CHN-900 instrument (Leco Corporation, St. Joseph, MI, USA). The combustion products (CO_2 and H_2O)

were analyzed quantitatively by infrared spectroscopy in order to determine the content of the elements.

Charge content

Carboxylate content was determined by electric conductivity titration method (Katz et al. 1984; Saito and Isogai 2004). 5 ml of NaCl at 0.01 M was added to 0.3 g of the nanofibers suspended in 85 ml of water under continuous stirring. Hydrochloric acid was added to the mixture to set the pH to 2.5–3, then the mixture was titrated by several additions of 200 μ l of 0.04 M NaOH solution while the electrical conductivity of the solution was measured. This was continued until the pH of the suspension reached 11. The negative charges content was determined from the middle line of the curve showing electrical conductivity versus volume of NaOH added. The degree of oxidation (DO) of TEMPO-oxidized cellulose nanofibers referring to the average number of carboxyls per anhydroglucose unit was calculated according to Eq. 1 (Perez et al. 2003).

$$DO = \frac{162 \cdot (V_2 - V_1) \cdot c}{w - 36 \cdot (V_2 - V_1) \cdot c} \quad (1)$$

where V_1 and V_2 are volumes of NaOH added for the neutralization of strong and weak acids, respectively. c is the NaOH concentration (mol l^{-1}), and w is the dry weight of the nanofibers.

The titration of the ChNF gives access to the ammonium content, and therefore the molar quantity of amine groups available for chelating metal ions (Fan et al. 2009). The TOChNF gives then a total charge content including the contribution of both carboxylic acids and ammonium groups (Fan et al. 2009).

Copper(II) adsorption onto the nanofibers

The copper adsorption capacity of biobased nanofibers was examined using the batch equilibrium method. 0.1 g of the nanofibers was mixed with 0.1–0.3 mmol of CuSO_4 with the total volume of the mixture being ca. 80 ml. The pH of the mixture was set to four different pHs (1.4, 3, 5, 6.2) by addition of diluted NaOH or HCl. This pH range was selected as it is widely used in the literature (Gurgel et al. 2008; Hokkanen et al. 2013). The mixture was magnetically

stirred overnight (for ca. 20 h), then vacuum filtered on top of a 0.65 μ m filter membrane (DVPP, Millipore). The DVPP membrane retained all nanofibers on top of it and did not adsorb copper and therefore could be used in these experiments. When the filtration was completed, the filtrate solution containing non-adsorbed copper was taken and weighed for further copper concentration determination by UV colorimetry (Silava 2010). The nanofibers with adsorbed copper retained on top of the membrane were subsequently washed several times by dipping in an aqueous solution having the same pH as the mixture after pH adjustment, and dried at room temperature for further XPS and WDX analyses.

Nickel(II), chromium(III) and zinc(II) adsorption onto the nanofibers

0.1 g of the nanofibers was mixed with 0.3 mmol of NiSO_4 , ZnCl_2 or CrNO_3 with the total volume of the mixture being ca. 80 ml. The pH of the mixture was set to six in the case of Ni and Zn and to pH five for Cr as heavy metal ions adsorption at those pH has been widely reported (O'Connell et al. 2008). The mixture was magnetically stirred overnight (for ca. 20 h), then vacuum filtered on top of a 0.65 μ m filter membrane (DVPP, Millipore). When the filtration was completed, the filtrate solution containing non-adsorbed metal ions was taken and weighed for further concentration determination by ICP-MS since UV colorimetry is not adapted for these heavy metal ions.

Determination of adsorbed heavy metal ions by the nanofibers

The Cu(II), Ni(II), Cr(III) and Zn(II) adsorbed onto the nanofibers was calculated by subtracting the amount of these heavy metal ions in the filtrate solution from their initial amount mixed with the nanofibers, and relating it to the dry weight of the nanofibers (0.1 g).

Copper adsorption onto montmorillonite nanoclay

Sodium montmorillonite (Cloisite Na^+ , Southern Clay Products) with a cation-exchange capacity (CEC) of 0.92 meq g^{-1} was exfoliated in water (0.1 g in 50 ml), then mixed overnight with 0.2 mmol of CuSO_4 with the total volume being 80 ml. The filtration method used for the nanofibers is not compatible with

Montmorillonite nanoclay due to the small size of the latter that passes through the filter, and a centrifugation method has been used instead. After centrifuging the Montmorillonite/Cu²⁺ mixture, the concentration of non-adsorbed copper in the supernatant solution could be determined by UV colorimetry, thus giving the amount of copper adsorbed onto the nanoclay.

Recycling experiments

Recycling experiments were performed by treating the contaminated nanofiber cake obtained after filtration with HCl. TOCNF.14 have been used as model nanofibers for this study (see Table 1). Adsorption of copper ions was first envisaged by mixing 0.25 g of TOCNF.14 with 0.375 mmol of CuSO₄ with the total volume of the mixture being ca. 100 ml and by adjusting the pH to six. After filtration of this suspension and determination of copper concentration in the filtrate, desorption experiments were performed by mixing TOCNF.14 retained on top of the filter with 20 ml of HCl at 5 wt% and completing the volume to ca. 200 ml with deionized water (the final pH of the solution was ca. 1.5). After filtration, the amount of desorbed copper was measured from the copper concentration in the filtrate knowing the amount of copper adsorbed during the same cycle.

XPS analysis

The spectra were acquired on a Physical Electronics (PHI) Quantum 2,000 photoelectron spectrometer using monochromated Al-K α radiation generated from an electron beam operating at 15 kV and

25 W, using the same parameters as described elsewhere (Tingaut et al. 2011). The binding energies of all spectra were shifted so that the O_{1s} signal is at 533.2 eV, the reference position for cellulose. Contributions of carbon (C_{1s}) and copper (Cu_{2p_{3/2}}) were detected at 285 and 933 eV, respectively. Surface elemental concentrations and Cu/C ratios were calculated from the low resolution survey spectra, using the predefined sensitivity factors in the MultiPak 6.1A software. Analysis of the XPS spectra was performed using the MultiPak 6.1A software provided by the instruments manufacturer, PHI.

WDX analysis

An X-ray map showing the distribution of copper on the sample surface was acquired using a wavelength-dispersive spectrometer (WDS). A 5 × 5 mm² film was fixed on a sample holder by using a carbon adhesive tape and then coated with carbon and examined using a scanning electron microprobe (JEOL JXA-8800RL) equipped with a wave-dispersive X-ray detector. An area of 300 × 300 μ m² was mapped using a 2 μ m step. The copper was detected at an accelerating voltage of 20 kV, a current of 20 nA, a focused electron beam, takeoff and tilt angles of 30° and 0°, respectively, and dwell (digital map) times of 80 ms/point.

Specific surface area

Prior to surface area measurements, biobased nanofibers were subjected to supercritical drying as reported elsewhere (Sehaqui et al. 2011b). The BET surface

Table 1 Notation, source, BET specific surface area (SSA) and average fibrils diameter (d) of CNF and ChNF according to their preparation method, charge content (CC) and degree of oxidation (DO) (Saito and Isogai 2004)

Notation	Source of nanofibers	Preparation method	CC ^a (mmol g ⁻¹)	DO	SSA (m ² g ⁻¹)	d (nm)
CNF	Pulp residue	Mechanical disintegration	0.10	0.01	229	11.6
TOCNF.04	Pulp residue	TEMPO oxidation	0.26	0.04	330	8.1
TOCNF.14	Pulp residue	TEMPO oxidation	0.86	0.14	267	10.0
TOCNF.21	Pulp residue	TEMPO oxidation	1.21	0.21	303	8.8
TOCNF.26	Pulp residue	TEMPO oxidation	1.50	0.26	345	7.8
ChNF	Crab shell	Mechanical disintegration	0.43	–	173	15.4
TOChNF	Crab shell	TEMPO oxidation	0.88	–	228	11.7

Note that TEMPO-oxidized cellulose nanofibers are denoted TOCNF_x, where x stands for the degree of oxidation

^a CC comprises COOH groups for unmodified and TEMPO-oxidized cellulose nanofibers, and both COOH and amine groups for unmodified and TEMPO-oxidized chitin nanofibers (Saito et al. 2007; Fan et al. 2009)

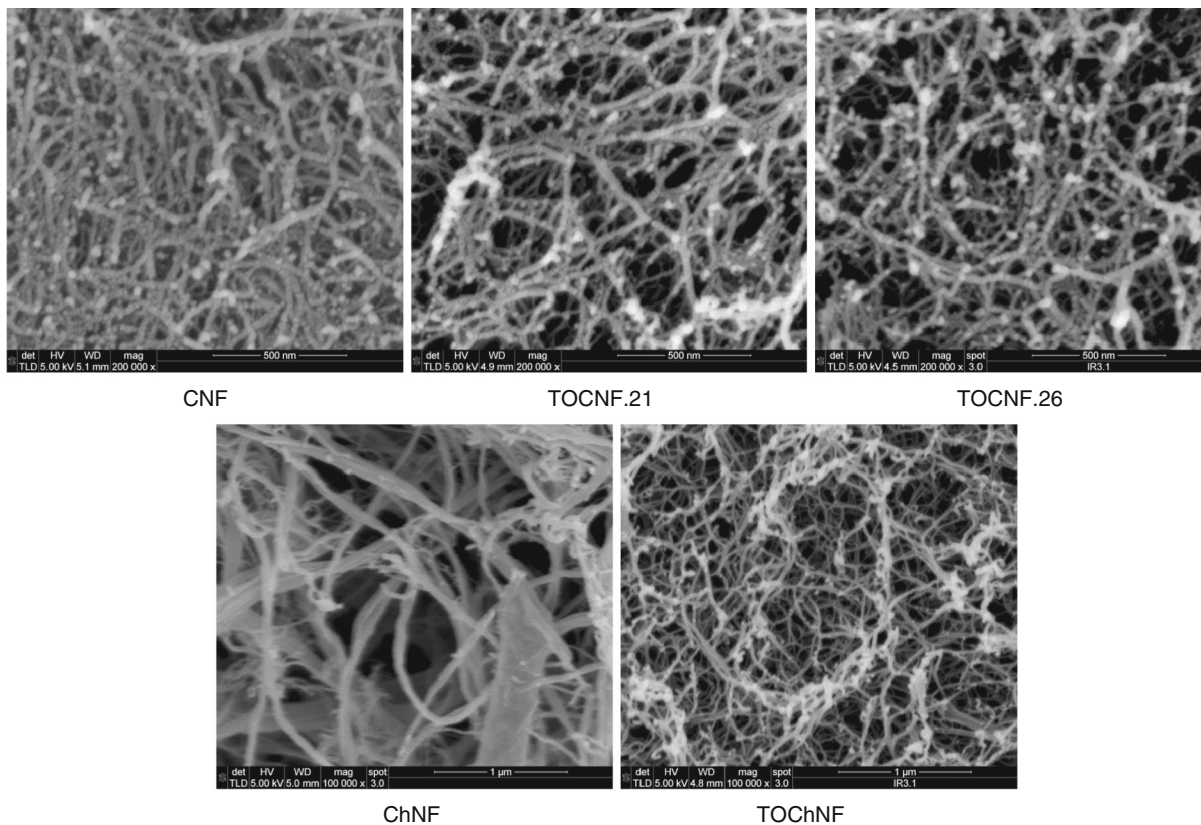


Fig. 1 SEM micrographs of the cellulosic nanofibers (*first row, scale bar is 500 nm*) and chitin nanofibers (*second row, scale bar is 1 micron*) envisaged in this study. The nomenclature is presented in Table 1

area was determined according to a multipoint BET method by nitrogen physisorption on a surface area and pore size analyser (Coulter SA3100). From BET specific surface area (SSA) values of the nanofibers, we estimated their corresponding average diameter d assuming they have a cylindrical shape using Eq. 2 and by taking $\rho = 1,500 \text{ kg m}^{-3}$ as density of CNF (Sehaqui et al. 2011a).

$$d = 4 / (\text{SSA} \cdot \rho) \quad (2)$$

Results and discussion

In the present study, we investigated the role of negative charges on the surface of different types of biobased nanofibers on their heavy metal ions removal capacity from contaminated water. Cellulose and chitin from wastes were selected as sources for the production of biobased nanofibers, and Cu(II), Ni(II), Cr(III) and Zn(II) as targeted heavy metal ions.

Table 1 presents the nomenclature and preparation methods of all aqueous nanofiber suspensions. The morphology of these nanofibers was characterized with SEM (Fig. 1). Typical network structure with high aspect ratio nanofibers is clearly visible for the fibrillated samples. Diameter of the nanofibrillated materials was mostly below 100 nm and smaller for TEMPO oxidized nanofibers (TOCNF, TOChNF) as compared with CNF and ChNF. SSA of biobased nanofibers ranged from 173 to $345 \text{ m}^2 \text{ g}^{-1}$. The average diameter of the fibrils back-calculated from their SSA was between 8 and 12 nm for cellulose and in the range of 12–15 nm for ChNF. The smallest diameters were measured for TEMPO-oxidized nanofibers (Table 1) thus supporting SEM observations and in agreement with the literature (Saito et al. 2007; Turbak et al. 1983; Sehaqui et al. 2011b). However, it should be noted that the present nanofibers are not monodisperse, and therefore a deviation from the average fibril diameter is expected.

Removal of Cu^{2+} using cellulosic nanofibers from pulp residue

In order to study the effect of surface carboxylate groups onto nanofibers copper adsorption, cellulose nanofibers having different DO were prepared from the pulp residue according to TEMPO-mediated oxidation method. Pulp residue is an attractive raw material since it is an inexpensive waste product from pulp and paper industry that could be exploited for the elaboration of new materials (Jonoobi et al. 2012; Spence et al. 2011). The reference CNF has been prepared by mechanical disintegration. Cellulose nanofibers with four different DO have been achieved and are denoted TOCNF_x with x referring to the DO (see Table 1).

The success of the oxidation reaction has first been assessed using FTIR–ATR spectroscopy (Fig. 2a). As compared with the spectrum of unmodified CNF, the characteristic vibrations of the carboxylate moieties were easily detected in the spectra of oxidized samples, namely the bands at $1,600\text{ cm}^{-1}$ ($\nu_{\text{as}}\text{COO}^-$) and $1,400\text{ cm}^{-1}$ ($\nu_{\text{s}}\text{COO}^-$). The intensity of these bands progressively increased with the DO, therefore confirming that the nanofibers were increasingly modified. This trend was also supported by elemental analysis and surface charges titration (Fig. 2b, c, respectively), for which the O/C ratio as well as the carboxylate content increased with the extent of the reaction, respectively.

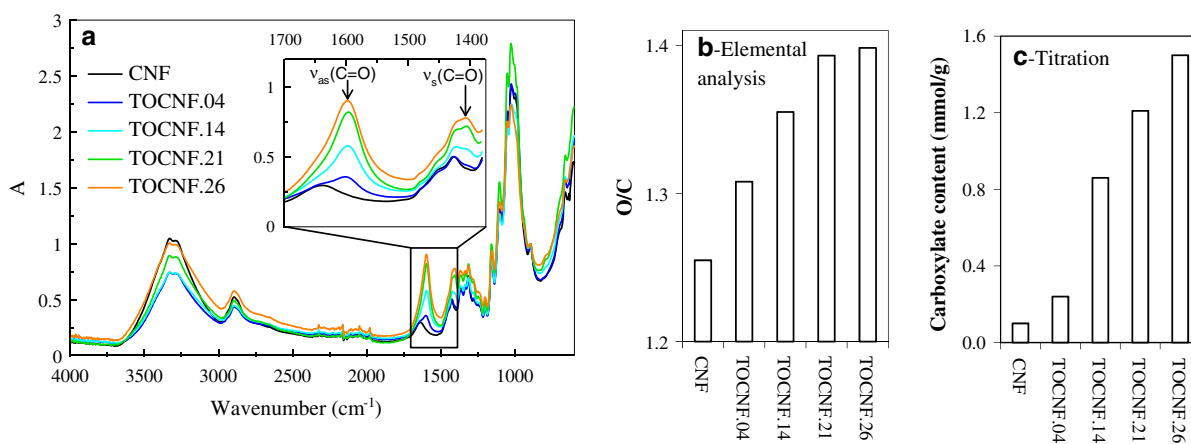


Fig. 2 a FTIR–ATR spectra of reference CNF and TEMPO-oxidized cellulose nanofibers from pulp residue (TOCNF). b Evolution of the O/C weight ratio of reference CNF and

The adsorption of copper ions (Cu^{2+}) onto unmodified and TEMPO-oxidized nanofibers from pulp residue was studied at four different pH's, namely, 1.4, 3, 5 and 6.2 (Fig. 3). For pH values above 6.2, copper precipitation was observed and therefore the study was limited to a maximum pH of ~ 6.2 . Results of copper adsorption onto nanofibers of different DO are shown in Fig. 3. Copper adsorption increased with the pH as well as with the DO with no noticeable copper adsorption at the lowest pH, in agreement with other studies (Gurgel et al. 2008; Hokkanen et al. 2013). Hence, in this acidic pH range, all carboxylic groups are protonated and can therefore not trap copper ions. When the pH increases, the proportion of carboxylic acid entities decreases to the benefit of their negatively charged carboxylates counterparts, these sites being favorable for copper(II) adsorption. Zeta potential measurements confirmed the negatively charged aspect of oxidized biobased nanofibers at higher pH (Zeta potential for TOCNF.26 was $\sim -50\text{ mV}$ at pH 7; See supplementary information S1). The iso-electric point of TOCNF.26 was ~ 1 and biobased nanofibers would have a negligible adsorption of heavy metal ions at such pH, in agreement with results in Fig. 3. Maximum Cu^{2+} adsorption values of 1.76 mmol g^{-1} (112 mg g^{-1}) and 0.21 mmol g^{-1} (13 mg g^{-1}) were measured for TOCNF.26 and the reference CNF respectively, thus clearly demonstrating the positive impact of carboxylate groups for Cu^{2+} adsorption. It should be noted that copper adsorption

TOCNF as determined by elemental analysis. c Carboxylate content of reference CNF and TOCNF as determined by titration

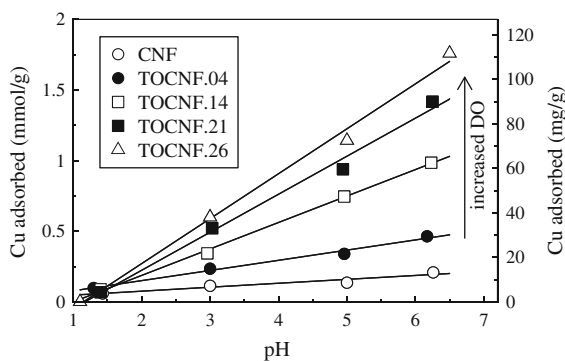


Fig. 3 Evolution of copper adsorption with pH onto cellulose nanofibers from pulp residue with different degrees of oxidation (DO). mmol g⁻¹ means mmol of copper adsorbed per gram of nanofibers

onto biobased nanofibers was linear and total when the copper amount mixed with the nanofibers was below the maximum adsorbable amount of Cu²⁺ by nanofiber, and reached a plateau for higher amounts of copper (See adsorption isotherm in supplementary information S2).

For further comparison, note that the amount of copper adsorbed by TOCNF.26 at pH ~6.2 was 1.5 times higher than that adsorbed at pH 5, and 2.9 times higher than that adsorbed at pH 3. Moreover, at pH ~6.2, TOCNF.26 adsorbed 1.8 times more copper than TOCNF.14.

A photograph of the nanofiber films after copper adsorption is presented in Fig. 4a. A turquoise color characteristic of copper(II) ions was observed on the surface of films and became more pronounced with increasing both, pH and DO values. This trend was associated with an increasing copper concentration on the surface of the films. This observation was further supported by the analysis of the surface chemical composition of selected samples after Cu²⁺ adsorption using XPS (Fig. 4b). The atomic Cu/C ratio increased with the pH and DO, with a maximum ratio of 0.036 calculated for TOCNF.26 at pH 6.2.

The impact of pH and DO on the distribution of Cu²⁺ on the surface of CNF, TOCNF.14 and TOCNF.26 films was further evaluated using WDX spectroscopy (Fig. 4c). Once again, a similar trend has been observed. Hence, the brightness of the copper map increased with the pH and DO values, indicating that the copper concentration on the surface of the films progressively increased. Moreover, the

distribution of copper was fairly homogeneous for all samples, as indicated by the relatively small standard deviations associated with each average Cu value (according to the arbitrary legend used in this Figure). Interestingly, a comparison of the average Cu values between samples implies that on the TOCNF.26 nanofiber film surface, the amount of copper adsorbed at pH 6.2 is 1.5 times higher than that adsorbed at pH 5 and 3.0 times higher than that adsorbed at pH 3. It also implies that TOCNF.26 adsorbs 1.9 times more copper than TOCNF.14 at pH ~6.2. Consequently, these observations are in very good agreement with previous results shown in Fig. 3, leading to the conclusion that the distribution of copper is homogeneous and similar at the surface and the bulk of the films.

The relationship between Cu²⁺ adsorption and the carboxylate content of different materials has then been evaluated, including for comparison purpose, highly oxidized cellulosic nanofibers prepared from high quality beech pulp fibers (TOCNF.34 having a carboxylate content of 1.95 mmol g⁻¹ and a DO of 0.34; see experimental section). The plot representing copper adsorption versus carboxylate content is presented in Fig. 5. For the 3 pHs studied, the copper(II) adsorption linearly increased with the carboxylate content, with the highest copper adsorption measured at pH of 6.2. The amount of copper atoms adsorbed per carboxylate group was then deduced from the slope of each curve, and were equal to 0.38, 0.70 and 1.05 at pH 3, 5 and 6.2 respectively. Consequently, the copper adsorption was almost equimolar to the carboxylates at pH ~6.2. From these results, it becomes apparent that the negative charges (carboxylates) onto the surface of the nanofibers are primarily responsible for copper(II) heavy metal ion adsorption. It should be noted that the influence of the SSA of different nanofibers on their heavy metal ions uptake was not investigated, and nanofibers with different SSA values may have different kinetics of heavy metal ions uptake.

These results also indicate that cellulose nanofibers isolated from the pulp residue have the same potential for water purification technology than cellulose nanofibers isolated from a high quality cellulosic raw material.

In a study by Saito et al., the capacity of TEMPO-oxidized cellulosic fibers to adsorb a wide range of metal ions was demonstrated (Saito and Isogai 2005).

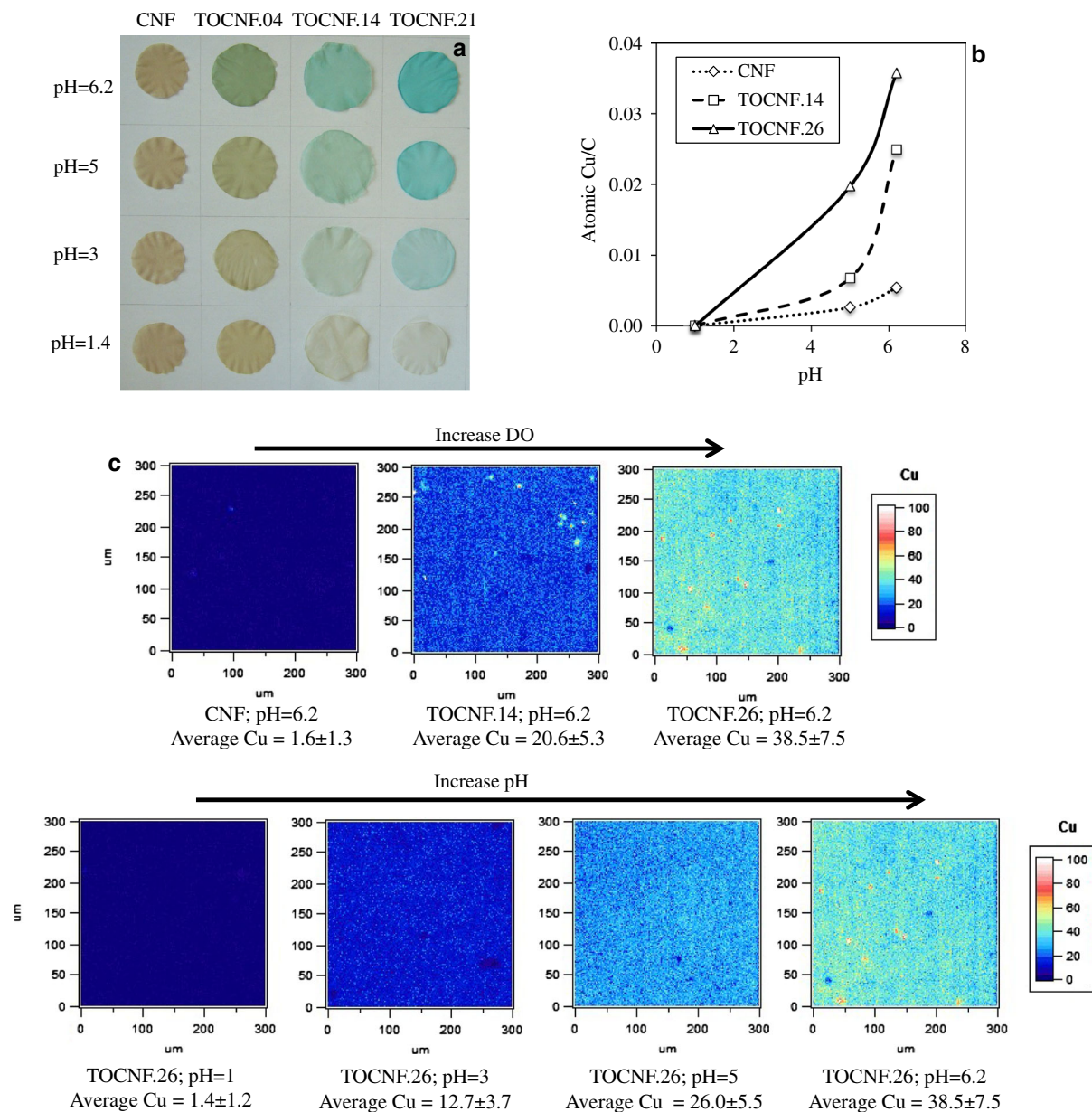


Fig. 4 **a** Photograph of nanofiber films after copper adsorption for different pH and nanofibers with different DO. **b** Atomic Cu/C ratio obtained by XPS analysis on nanofiber films after copper adsorption. **c** WDX map ($300 \times 300 \mu\text{m}^2$) showing the

distribution of copper on the surface of nanofiber films. Average Cu corresponds to the average copper value of the sample calculated from each pixel in the copper map according to the arbitrary scale in right

The fibers possessed a carboxylate content of 0.48 mmol g^{-1} and could adsorb ca. 0.36 mmol g^{-1} of Cu^{2+} at pH ~ 3.5 . In our study, TOCNF.34 nanofibers adsorb a higher copper amount at similar pH (0.88 mmol g^{-1} at pH 3), and this is mainly due to the higher carboxylate content of TOCNF.34

(1.95 mmol g^{-1}). Furthermore, the advantage of using TEMPO-oxidized nanofibers instead of fibers counterparts is related to the higher SSA of the former (above $250 \text{ m}^2 \text{ g}^{-1}$; see Table 1) which should result in a faster kinetic of copper adsorption. The fast adsorption of copper ions onto nanofibers has been

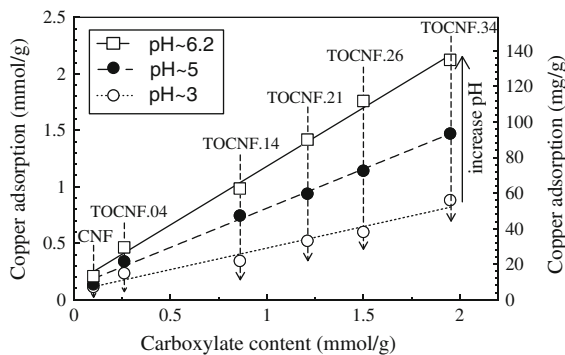


Fig. 5 Copper adsorbed versus carboxylate content for reference nanofibers (CNF) and TEMPO-oxidized nanofibers (TOCNF) from the pulp residue. The sample TOCNF.34 has been produced after oxidation of beech pulp and is placed for comparison purpose

shown by a kinetic study on TOCNF.26 that showed that 93 % of the maximum copper adsorption capacity was achieved within the first 10 s of the mixing of Cu^{2+} with TOCNF.26 while no considerable change in copper adsorption was observed beyond 100 s of mixing (supplementary information S3).

While activated carbon is the most used sorbent for heavy metal ions removal from wastewater, many researchers are seeking cheap and efficient alternatives to this material due to its high production cost. Amongst them are natural nanoclays considered as low-cost and highly efficient adsorbents (Veli and Alyuz 2007; Celis et al. 2000; Lothenbach et al. 1997). It is therefore relevant to compare heavy metal ions removal capacity of the present nanofibers to that achieved by nanoclays. Montmorillonite (cloisite- Na^+) with high (CEC of 0.92 meq g^{-1}) has been selected for this purpose. As shown in Fig. 6, the present oxidized cellulose nanofibers could have up to 2.4 times higher copper adsorption capacity than Montmorillonite nanoclay (copper adsorbed by Montmorillonite at pH 6.2 is 0.9 mmol g^{-1} equivalent to 57 mg g^{-1}). Consequently, the carboxylate groups onto cellulose nanofibers surface would have similar function in terms of copper adsorption than cation exchanges by Montmorillonite nanoclay and could potentially replace them for heavy metal ions removal from wastewater. A comparison with literature work shows that the present oxidized nanofibers perform better in terms of copper adsorption than many other sorbents from biobased resources including aspen wood fibers (4 mg g^{-1}) (Huang et al. 2009), sawdust

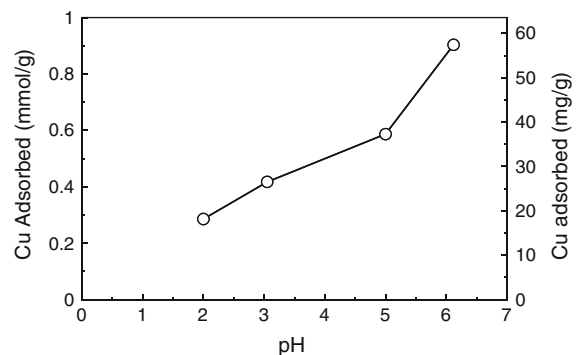


Fig. 6 Evolution of copper adsorption with pH onto Montmorillonite nanoclay

(1.79 mg g^{-1}) (Yu et al. 2000), sugar beet pulp ($0.333 \text{ mmol g}^{-1}$) (Reddad et al. 2002), wheat (17.422 mg g^{-1}) (Aydin et al. 2008), wheat bran (51.5 mg g^{-1}) (Ozer et al. 2004), modified jute fibers (8.4 mg g^{-1}) (Shukla and Pai 2005), herbaceous peat (4.84 mg g^{-1}) (Gundogan et al. 2004), carbonarius biomass (19.47 mg g^{-1}) (Alasheh and Duvnjak 1995), untreated and pretreated marine algae ($6.12 \text{ mmol kg}^{-1}$) (Pavasant et al. 2006), (38.2 mg g^{-1}) (Lee and Chang 2011), (1.3 mmol g^{-1}) (Matheickal and Yu 1999), bentonite clay (44.84 mg g^{-1}) (Veli and Alyuz 2007), kaolinities ($\sim 20 \text{ mmol kg}^{-1}$) (Suraj et al. 1998), and have similar or lower copper adsorption capacity than a mercerized cellulose modified with succinic anhydride (139 mg g^{-1}) (Karnitz et al. 2007), (153.9 mg g^{-1}) (Gurgel et al. 2008).

Besides the high metal binding capacity of biobased nanofibers, it is interesting to consider the possibility to recycle the nanofibers after metal adsorption. Here, we subjected TOCNF.14 (chosen as model nanofibers) to three copper adsorption–desorption cycles and evaluated the evolution of their performances upon recycling experiments (Fig. 7). The regeneration was performed in acid medium since cellulose nanofibers have a low Cu^{2+} binding capacity at low pH (see Fig. 3). Under the conditions used in our study, 73 % of total Cu^{2+} adsorbed by TOCNF.14 could be desorbed in the first desorption cycle, while 65 and 61 % could be desorbed in the second and third desorption cycles, respectively. Moreover, ~ 90 % of the maximum adsorption capacity by TOCNF.14 nanofibers in the first cycle was achieved by TOCNF.14 in the second and third adsorption cycles. These results suggest the recycling capability of the

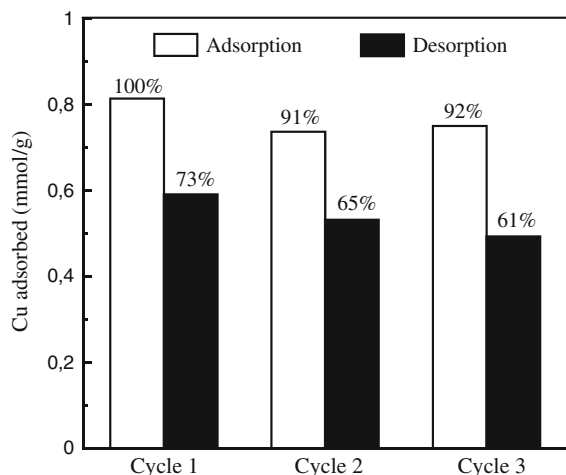


Fig. 7 Copper adsorption–desorption cycles onto TOCNF.14. Adsorption is carried out at pH 6. Percentages refer to the amount of Cu^{2+} adsorbed/desorbed related to the first adsorption value

nanofibers for their reuse in heavy metal ions capture, and are in agreement with a recent study on the recycling of oxidized regenerated cellulose where most of copper adsorbed onto regenerated cellulose hydrogel could be desorbed after HCl treatment (Isobe et al. 2013). Further investigations will aim at reaching a 100 % recovery yield with our protocol. After removal of heavy metal ions from nanofibers, a concentrated solution of heavy metal ions would be obtained and this may be exploited for the metal recovery when it is precious, or in other applications involving metal ions in water such as electrochemistry. The adsorbent on the other hand may be incinerated or recycled. Our ongoing and planned research evaluates these factors and will be reported in future.

Removal of Cu^{2+} using ChNF

The capacity of unmodified and TEMPO oxidized (ChNF and TOChNF, respectively) to trap Cu^{2+} was also evaluated (Fig. 8). For all pHs envisaged in the study, the highest copper adsorption capacity has been measured for the TOChNF which was expected due to their high surface charge content (0.88 mmol g^{-1} , see Table 1). The highest copper adsorption measured for TOChNF was still lower than the maximum adsorption capacity achieved for oxidized cellulose nanofibers (135 mg g^{-1} for TOCNF.34 vs. 55 mg g^{-1} for TOChNF at pH ~ 6.2), which was expected due to the

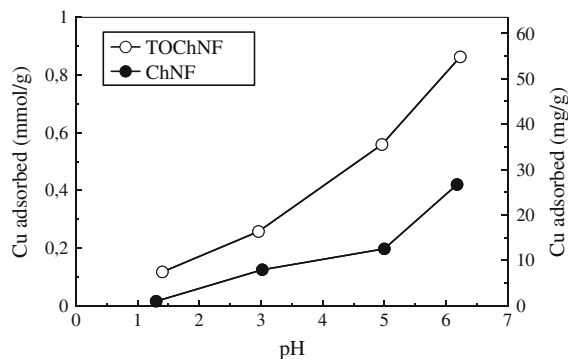


Fig. 8 Evolution of copper adsorption onto chitin nanofibers (ChNF), and TEMPO-oxidized chitin nanofibers (TOChNF) as function of pH

lower charge content of oxidised chitin nanofibers. The reference nanofibers on the other hand showed a higher adsorption capacity for ChNF (27 mg g^{-1}) compared to CNF (13 mg g^{-1}). The structural difference between cellulose and chitin may be the reason since surface complexes of Cu^{2+} with the C2 amine groups in chitin may be formed.

The maximum copper adsorption capacity measured for TOChNF (0.86 mmol g^{-1}) was higher than copper adsorbed onto partially deacetylated prawn shell (0.27 mmol g^{-1}) (Chu 2002) chitosan flakes (0.33 mmol g^{-1}) (Bassi et al. 2000) or chitosan powder (0.71 mmol g^{-1}) (Huang et al. 1994), but lower than copper adsorption onto cross-linked chitosan beads (3.71 mmol g^{-1}) (Lee et al. 2001), crab shell particles (244 mg g^{-1}) (Vijayaraghavan et al. 2006), and chitosan flakes (2.75 mmol g^{-1}) (Wu et al. 1999).

Removal of Ni^{2+} , Cr^{3+} and Zn^{2+} using TEMPO-oxidised cellulose nanofibers

Since we have previously highlighted the strong potential of TEMPO-oxidized nanofibers for the removal of copper metal ions from water, the ability of these nanofibers to adsorb other heavy metal ions, namely Ni(II), Cr(III) and Zn(II) was subsequently investigated by ICP-MS. For this study, we used the oxidized nanofibers from the pulp residue with the highest DO, namely TOCNF.26, as these nanofibers could be exploited as low-cost sorbent from waste product. ICP-MS has been envisaged for the quantification of metal ions in the filtrate and subsequent evaluation of the metal adsorption by the nanofibers

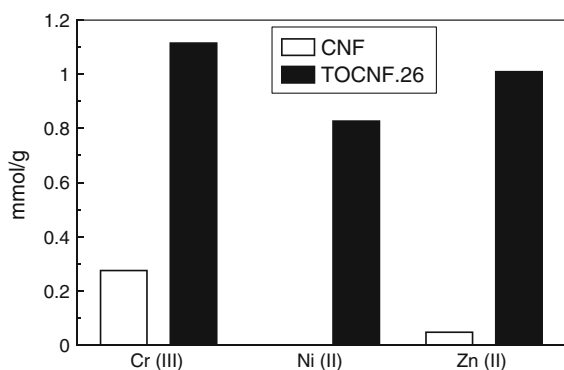


Fig. 9 Adsorption of Cr(III), Ni(II) and Zn(II) onto CNF and TOCNF.26 at a pH of the mixture of five for Cr(III) and six for Ni(II) and Zn(II)

since UV spectroscopy is not suitable for these metals. Results are presented in Fig. 9 and show that TOCNF.26 has a higher adsorption capacity for these metal ions than unmodified CNF. Adsorption values towards Cr, Ni and Zn ions were 58, 49 and 66 mg g⁻¹ respectively (corresponding to 1.1, 0.8 and 1.0 mmol g⁻¹, respectively). This is amongst the best low-cost sorbents compared to those reported in review articles (Babel and Kurniawan 2003; Ngah and Hanafiah 2008). When several heavy metal ions are simultaneously present, adsorption of heavy metal ions by nanofibers would be different from the present case where a single heavy metal ion is in contact with the nanofibers and a thorough selectivity study should be made. In conclusion, TEMPO-modified nanofibers from the pulp residue seem to have a wide spectra of heavy metal ions removal capability and could effectively be used as natural adsorbent for water treatment.

Conclusion

Biobased nanofibers from the most abundant polymers i.e., cellulose and chitin, have been prepared from two waste materials, namely the pulp residue and crab shell. The influence of their surface charge content (carboxylates) on their performance as heavy metal ions sorbents has been investigated. Four metal ions have been studied in this work: Cu(II), Ni (II), Cr(III) and Zn (II). Reference nanofibers prepared by mechanical disintegration of cellulose (CNF) and chitin (ChNF) sources had a relatively low amount of

negative charges on their surface resulting in low Cu²⁺ adsorption capacities. A higher adsorption value has been measured for reference chitin nanofibers as compared with cellulose nanofibers (27 mg/g for ChNF vs. 13 mg/g for CNF) and has been attributed to presence of C2 amine groups in chitin. Introducing carboxylates groups onto the surface of the nanofibers through TEMPO-mediated oxidation proved to be a facile functionalization route that enhanced considerably their copper adsorption through electrostatic interactions. Copper adsorption onto nanofibers increased linearly with the carboxylate content and pH since H⁺ competes with Cu²⁺ for adsorption onto nanofibers at acidic conditions leading to an uncharged character of the nanofibers (also confirmed by Zeta potential measurements). A maximum carboxylate content of 1.95 mmol g⁻¹ onto highly oxidized cellulose nanofibers led to about an equimolar adsorption of copper (2.1 mmol g⁻¹ equal to 135 mg g⁻¹). The high surface area of the nanofibers resulted in a fast adsorption of copper onto the biobased nanomaterials in the order of a minute. The much lower carboxylate content achieved on oxidized chitin nanofibers (TOChNF) compared to that achieved on oxidized cellulose nanofibers (TOCNF) resulted in a lower copper adsorption capacity of 55 mg g⁻¹ onto TOChNF. TEMPO-oxidised nanofibers from the pulp residue could also adsorb other heavy metal ions as demonstrated with Ni (II), Cr(III) and Zn (II), and heavy metal ions could be desorbed from nanofibers through an acidic washing so that nanofibers could be reused. The green and abundant aspects of the waste bioresources envisaged in this work, their good performance in terms of heavy metal ions adsorption, and the possibilities to recycle them after use are strong arguments to consider them as sorbents for heavy metal ions removal from contaminated water.

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