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Bisphosphonate nanocellulose in the removal of vanadium(V) from water

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Abstract Due to environmental concerns and decreasing global resources, removing aqueous heavy metals from industrial wastewaters is important for ecological sustainability. In this work, the removal of vanadium from a synthetic aqueous solution using bisphosphonate nanocelluloses was studied. Bisphoshonate nanocellulose was obtained from periodate oxidized and sodium alendronate aminated wood cellulose fibers using a mechanical disintegration method. Depending on the reaction condition, long flexible nanofibrillated celluloses or shorter rigid cellulose nanocrystals (CNCs) were obtained. The most efficient removal of vanadium was obtained at low solution pH (2 and 3), which is most likely due to the complexation of vanadium with bisphosphonate groups and the electrostatic interaction between cationic vanadium species and anionic acid groups. Based on the Langmuir isotherm, a maximum adsorption capacity of 1.98 mmol/g was attained with the CNCs that had 0.32 mmol/g of bisphosphonate content. The adsorption kinetic of vanadium was modeled and found to follow a pseudo-second-order model.

Keywords Nanocellulose · Periodate · Bisphosphonate · Metal removal · Vanadium

Introduction

Heavy metal pollutants are some of the most potent hazards for the environment as they can accumulate in biosystems because these pollutants are non-biodegradable (Bailey et al. 1999). Although several heavy metals are essential dietary minerals (micronutrients) for numerous organisms, including humans, heavy metals are mostly required in minute quantities and can exhibit significantly high toxicity even at low concentrations (Rengel 1999), and the limit between biological demand and toxicity can be narrow, depending on the metal species. Therefore, efficient recovery and recycling of heavy metals provide environmental benefits and could help decrease the impending shortage since many heavy metals are valuable substances with many applications.

Vanadium is an essential dietary mineral, for example, in the growth of rats (Schwarz and Milne 1971), that, however, is also toxic at very low concentrations and therefore is in the same class as mercury, lead, and arsenic (Lazaridis et al. 2003). Based in animal studies, the daily requirement of

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vanadium is 20 µ/day, whereas as low level as 60 mg/kg/day of vanadium(V) has been shown to exhibit reproductive toxicity to rats (Domingo 1996). The toxicity of vanadium depends on its oxidation state; +V has the highest toxicity. The oxidation state of +V is also the most stable form in a water solution and can exist as anionic, cationic, and neutral species (Naeem et al. 2007). Industrial use of vanadium is the source of vanadium found in waste waters. Due to its high tensile strength, hardness, and fatigue resistance, vanadium is used in ferrous and non-ferrous alloys (Moskalyk and Alfantazi 2003). Vanadium is also used as a catalyst in manufacturing sulfuric acid (Eriksen et al. 1995) and as an oxidizer in the production of maleic anhydride (Abon and Volta 1997).

Nanosized materials such as inorganic metal nanoparticles (Cai et al. 2010), carbon nanotubes (Stafiej and Pyrzynska 2007), and hybrid nanomaterials (Liu et al. 2009; Chen et al. 2011) have previously been investigated as potential adsorbents for removing miscellaneous toxic pollutants from water. Compared to larger counterparts, nanomaterials have a very high surface area, which leads to efficient interaction with pollutants. One potential biobased nanoadsorbent material is nanocellulose, which has a surface area of several hundred square meters per gram (Dufresne 2013). Cellulosic materials possess a high number of reactive hydroxyl groups that can be converted to more specific adsorption sites (e.g., different anionic or cationic groups) (Habibi 2014). Compared to many inorganic materials, nanocelluloses are biodegradable (Klemm et al. 2011), have low toxicity (Alexandrescu et al. 2013; Pitkänen et al. 2014), and are produced from abundant and renewable sources (natural cellulose fibers). Depending on the fabrication method, producing nanocellulose has a similar or even lower total environmental impact (e.g., consumption of energy during the production) than other nanoparticles (Arvidsson et al. 2015).

Nanocelluloses can be produced with several methods. Long nanofibrillated celluloses (NFCs) are typically fabricated using the mechanical disintegration of non-modified (Herrick et al. 1983) or chemically (Saito et al. 2006), enzymatically (Henriksson et al. 2007), and solvent-treated (Carrillo et al. 2014; Sirviö et al. 2015a) cellulose fibers. Shorter cellulose nanocrystals (CNCs) can, in turn, be obtained with acid hydrolysis or oxidative treatment of natural fibers (Rånby et al. 1949; Leung et al. 2011; Visanko et al. 2014). Previously active adsorption groups have been introduced on nanocelluloses using post-chemical treatments (Hokkanen et al. 2013; Jebali et al. 2014; Suopajärvi et al. 2015; Liu et al. 2015). However, this approach requires cumbersome purification steps for nano-sized cellulose, and therefore, more straightforward modification methods are desired. We have previously shown that bisphosphonate nanocelluloses (NFCs or CNCs, depending on the initial degree of oxidation) can be obtained using combined periodate oxidation and reductive amination with sodium alendronate pretreatment followed by mechanical disintegration. Anionic bisphosphonate groups, which are introduced on the cellulosic fiber raw material, enable the efficient liberation of nanocelluloses by creating electrostatic repulsion between natural cellulose fibers and promoting amorphous cellulose dissolution. Since the bisphosphonate groups are efficient chelation groups for vanadium (Crans et al. 2007), in the present study bisphosphonate nanocelluloses were used to remove vanadium(V) from synthetic water. The role of solution pH, contact time, nanocellulose dosage, and initial vanadium concentration were addressed in particular. The adsorption kinetics and isotherms of vanadium were determined to study the adsorption mechanisms of bisphosphonate nanocelluloses.

Experimental

Materials

Bleached birch pulp (*Betula pendula*) was obtained as dry sheets and used as the cellulose material after the pulp had disintegrated in deionized water. The properties of cellulose are presented elsewhere (Liimatainen et al. 2011). Amount of vanadium in cellulose pulp was <1 mg/kg.

Chemicals used in periodate oxidations ($NaIO_4$, LiCl), reductant in amination ($C_6H_7N{\cdot}BH_3$), and aldehyde and carboxyl content analyses ($NH_2OH{\cdot}HCl$, $CH_3COONa{\cdot}2H_2O$, NaCl, and NaOH) were obtained as p.a. grade from Sigma-Aldrich (Germany). Sodium alendronate trihydrate ($C_4H_{12}NaNO_7P_2{\cdot}3H_2O$) used in phosphonation was obtained from TCI (Germany). Uranyl acetate used in the transmission electron microscopy (TEM) images was obtained from Polyscience (Germany). Sodium metavanadate ($NaVO_3$, Sigma-Aldrich) was used as the vanadium source in the adsorption studies.

Deionized water was used throughout the experiments except during the preparation of the TEM samples, when ultrapure water (ISO 3696, Grade 1) was used.

To measure the charge density of nanocelluloses with polyelectrolyte titration, 0.1/1 M NaOH and HCl (Merck), NaH_2PO_4 (Sigma-Aldrich), $NaNO_2$ (Sigma-Aldrich), NaCOO (Sigma-Aldrich), $NaCH_3COO$ (Oy FF Chemicals), Na_2HPO_4 (Sigma-Aldrich), $NaHCO_3$ (Merck), and Na_2CO_3 (Sigma-Aldrich) were used to prepare buffers and used without further purification. Poly(diallyldimethylammonium chloride) (PolyDADMAC, BTG Mütek GmbH, Germany) was used as a titrant without further purification.

Fabrication of bisphosphonate nanocelluloses

Bisphosphonate nanocelluloses were fabricated by the method published previously (Sirviö et al. 2015b). Briefly, 12 g of cellulose was oxidized with $NaIO_4$ at 55 °C (DAC 1), 65 °C (DAC 2), and 75 °C (DAC 3 and 4). LiCl (21.6 g) was used as an additive with a suspension of DAC 4. Aldehyde content of DAC 1, DAC 2, DAC 3, and DAC 4 were 1.68, 2.20, 2.84, and 3.83 mmol/g, respectively. Then 9.0 g of DAC was allowed to react with 10X molar excess of sodium alendronate in the presence of 2X molar excess of 2-picoline borane for 72 h. Bisphosphonate celluloses (0.5 % dispersion at pH of 10) were then disintegrated into nanocelluloses using a high-pressure homogenizer (APV-2000, Denmark) with the following pressure: 250, 500, 570, and 1050 bars (BPNC1), 500, 570, and 1050 bars (BPNC2 and BPNC3), and 680 and 1050 bars (BPNC4).

Transmission electron microscopy

The morphological features of the fabricated nanocelluloses were analyzed with a Tecnai G2 Spirit transmission electron microscope (FEI Europe, Netherlands). Samples were prepared by diluting each sample with ultrapure water. A small droplet of the dilution was dosed on top of a Butvar-coated copper grid. An excess amount of the sample was removed from the grid by touching the droplet with a corner of a filter paper. Negative staining of the samples was performed by placing a droplet of uranyl acetate (2 % w/v) on top of each specimen. Excess uranyl acetate was removed with filter paper, as described. Grids were dried at room temperature and analyzed at 100 kV under standard conditions. Images were captured with a Quemesa CCD camera.

Polyelectrolyte titration

The polyelectrolyte titrations were performed with a Mütek PCD 03 particle charge detector (Mütek Analytic, Germany). Aqueous 1 meq/dm^3 polyDADMAC was added to the buffered nanocellulose suspensions while the sign of the sample charge was monitored.

Batch adsorption experiments

The batch experiments were conducted at room temperature by shaking the desired amount of nanocelluloses with the synthetic vanadium solution (25 or 50 ml) with the desired concentration of vanadium in a plastic bottle in a shaker for 1–24 h, after which the sample was filtered using a 0.2 µm polyethersulfone membrane. First, 10 ml was removed for the vanadium analyses. The samples (10 ml) for the vanadium analysis were preserved with 30 % HCl (Suprapur, 50 µl/10 ml). Vanadium was analyzed with graphite furnace atomic absorption spectrophotometry (Perkin Elmer AAnalyst 600) with argon (SFS 5074).

Adsorption kinetics

Pseudo-first-order and pseudo-second-order kinetics were employed to describe the kinetics of the adsorption of the vanadium on bisphosphonate nanocellulose. The pseudo-first-order kinetic model is shown in Eq. (1) (Namasivayam and Sangeetha 2006):

$$\frac{t}{q_t} = \frac{k_1}{q_e t} + \frac{1}{q_e} \tag{1}$$

where k_1 (1/min) is the rate constant of the pseudo-first-order adsorption, and q_t and q_e are the metal ion amounts adsorbed at time t (min) and equilibrium, respectively. The pseudo-second-order kinetic model is shown in Eq. (2) (Ho and McKay 1998):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right)t \tag{2}$$

where k_2 (g/mmol/min) is the rate constant of the pseudo-second-order adsorption.

Adsorption isotherms

The adsorption mechanisms were studied using Langmuir and Freundlich isotherm models. A linear form of the Langmuir isotherm is shown in Eq. (3) (Namasivayam and Sangeetha 2006):

$$\frac{C_e}{q_e} = \left(\frac{1}{bQ_0}\right) + \left(\frac{C_e}{Q_0}\right) \tag{3}$$

where C_e is the equilibrium concentration of the adsorbate in the solution (mmol/l), q_e is the adsorbed amount (mg/g) at equilibrium, b (l/mmol) is a Langmuir constant that is related to the affinity of the binding sites, and Q_0 is the maximum adsorption capacity for monolayer formation on the adsorbent.The separation factor, R_L, that describes the affinity between the absorbate and the adsorbent is shown in Eq. (4) (Gadd 2009; Gupta and Babu 2009):

$$R_L = \frac{1}{1 + bC_0} \tag{4}$$

where C_0 is the initial metal ion concentration.

The logarithmic form of the Freundlich isotherm is shown in Eq. (5) (Namasivayam and Sangeetha 2006):

$$\log q_e = \log K_f + \frac{1}{n}(\log C_e) \tag{5}$$

where K_F ($(\mathrm{mg}^{1-n}/\mathrm{gL}^n)$) and *n* (dimensionless) represent the Freundlich constants.

Results and discussion

Bisphosphonate nanocellulose

Bisphosphonate celluloses were fabricated from wood cellulose fibers by first oxidizing them to dialdehyde cellulose (DAC) with sodium metaperiodate followed by reductive amination using sodium alendronate as a bisphosphonate containing amine. 2-picoline borane, which has moderately low reduction efficiency, was used as a reductant during the amination reaction as this agent is a safer alternative to many other reductants, such as sodium borohydride and sodium cyanoborohydride (Dangerfield et al. 2010). Nanocelluloses were liberated from chemically modified fibers by subjecting them to mechanical disintegration with a high-pressure homogenizer. BPNC1 existed mainly as long individual nanofibrils while BPNC2 appeared as a mixture of nanofibrils and nanocrystals. BPNC3 and BPNC4 mainly consisted of short nanocrystals. An example of the TEM images of the samples is in Fig. 1. The bisphosphonate content and charge density as a function of pH are presented in Table 1.

Vanadium removal

Batch experiments with model solutions that contained aqueous metals were used to evaluate the efficiency of bisphosphonate nanocellulose in removing vanadium. The removal efficiency is presented as a function of pH in Fig. 2. At acidic pH (2 and 3), the bisphosphonate nanocelluloses exhibited adsorption capacities of 0.17–0.21 mmol/g when the initial vanadium concentration of 0.24 mmol/l was used (Fig. 2). Adsorption capacity was significantly decreased at neutral and basic pH. This effect is likely associated with the pH dependency of the vanadium charge. Vanadium can exist as cationic, neutral, and anionic species at acidic pH depending on the initial metal concentration (Peacock and Sherman 2004), whereas at higher pH, different multicharged anions are present. Because all nanocelluloses exhibited an anionic charge at the pH range 3–10 (Table 1), the adsorption of vanadium is most likely based on the complexation of vanadium with bisphosphonate groups (Crans et al. 2007) and the electrostatic interaction between the cationic vanadium species and the anionic acid groups. Moreover, the cationic secondary amino groups of the nanocelluloses likely interact with anionic vanadium species at low pH. The decrease in adsorption capacity at high pH is most likely due to the increase in the anionic charge of nanocellulose and the absence of cationic vanadium species resulting in electrostatic repulsion between the nanocelluloses and anionic vanadium. Previously, cationic adsorbents such as quaternized cellulose (Anirudhan et al. 2009) and crosslinked chitosan (Qian et al. 2004) were also found to adsorb vanadium at low pH (3–6). In these cases, the adsorption is likely mainly based on the electrostatic interaction between the cationic adsorbent and the anionic vanadium species.

Since the sorption was more efficient at very low pH, additional experiments were conducted at pH 3. The kinetics of vanadium removal is presented in Fig. 3. For

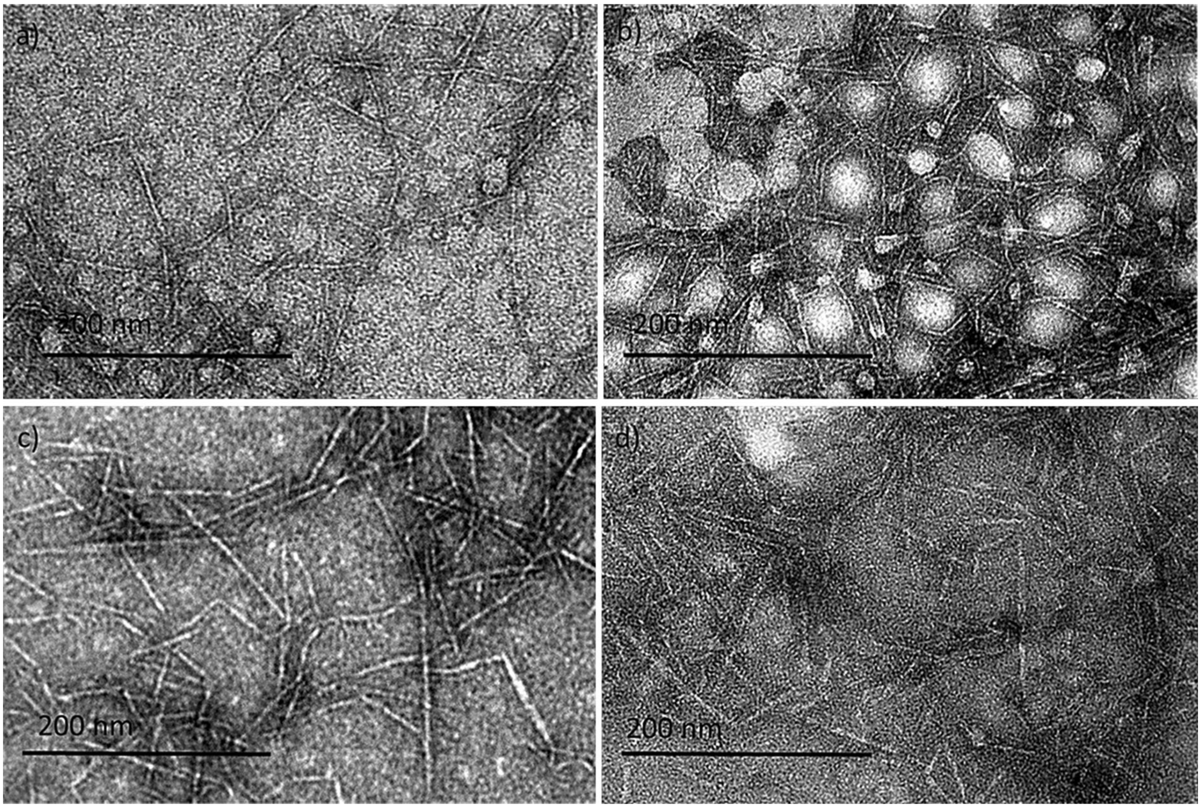

Fig. 1 TEM images of bisphosphonate nanocelluloses **a** BPNC1, **b** BPNC2, **c** BPNC3, and BPNC4

Table 1 Bisphosphonate content and charge densities of bisphosphonate celluloses

Nanocellulose sample	Bisphosphonate group content (mmol/g)	Charge density (meqv/g)			
		pH 3	pH 5	pH 7	pH 10
BPNC1	0.17	−0.22	−0.30	−0.53	−0.69
BPNC2	0.22	−0.41	−0.53	−0.91	−1.27
BPNC3	0.29	−0.31	−0.54	−0.86	−1.16
BPNC4	0.32	−0.63	−0.87	−1.51	−1.99

all samples, a rapid initial increase in vanadium removal was obtained during the first 60 min, after which the adsorption capacity was constant or increased more slowly. An adsorption plateau was observed for BPNC4 after 24 h, while the other samples showed a gradual increase in adsorption capacity after 24 h. Rabid initial adsorption is typical to many vanadium adsorbents. For example, chitosan-zirconium(IV)composite and amine-modified poly(glycidyl methacrylate)-grafted cellulose showed adsorption plateau around 60 min, which is similar to BPNC4. The kinetic constant parameters of the pseudo-first- and second-order kinetics can be seen in Table 2. The adsorption kinetics followed the pseudo-second-order kinetic model (e.g., R^2 for BPCN2 was 0.7300 and 0.9998 for the pseudo-first- and second-order kinetics), which is consistent with previous results for vanadium adsorption on activated carbon (Namasivayam and Sangeetha 2006). Since the pseudo-second-order kinetic model is based on the assumption that chemisorption is the rate-controlling step (Ho 2006), the adsorption of vanadium may be a chemical-controlling process (Wang et al. 2012), and sorption involves valency forces through sharing or exchange of electrons between bisphosphonate nanocelluloses and vanadium

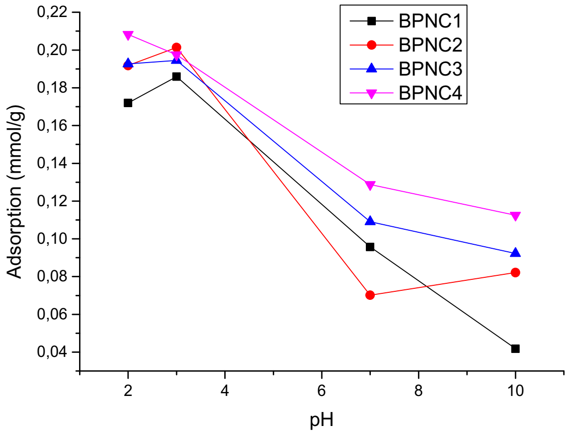

Fig. 2 Effect of initial solution pH on the vanadium adsorption. Conditions: 0.24 mmol/l of vanadium; 1 g/l of nanocellulose; 24 h shaking time; volume of 50 ml; room temperature

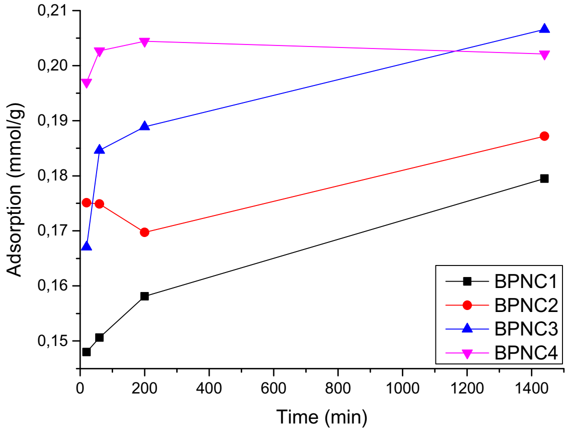

Fig. 3 Effect of contact time on the vanadium adsorption. Conditions: 0.22 mmol/l of vanadium; 1 g/l of nanocellulose; pH 3; volume of 50 ml; room temperature

(Ho and McKay 1999). The calculated adsorption capacities were similar to those obtained from the experimental results.

It was observed that BPNC4 had the highest adsorption capacity at the lowest nanocellulose concentration (Fig. 4). Using 0.2 g/l of BPNC4, 80 % of vanadium was removed when the initial vanadium concentration was 0.23 mmol/l, and only a minor increase was observed when the nanocellulose concentration was increased. However, when the other bisphosphonate nanocelluloses were used, the adsorption capacity was increased by the increase in the nanocellulose concentration, and the maximum was observed with 0.74–1 g/l.

The dependency of the adsorption capacity on the initial vanadium concentration is presented in Fig. 5. Clear differences in adsorption capacities were obtained for the bisphosphonate nanocelluloses. BPNC1 had the lowest adsorption capacity of the entire vanadium concentration range. At the maximum vanadium concentration (3.58 mmol/l), the experimental maximum adsorption capacities (q_e (exp)) were 0.92, 1.15, 1.34, and 1.67 mmol/g for BPNC1, BPNC2, BPNC3, and BPNC4, respectively. These results are in logical order based on the bisphosphonate content of the nanocelluloses.

Langmuir and Freundlich isotherms were used to model vanadium adsorption on bisphosphonate nanocelluloses (Table 3). Of the isothermic models, a better fit was obtained with a Langmuir isotherm for BPNC1, BPNC2, and BPNC4 ($R^2 = 0.992$–0.997 vs. 0.878–0.912). In the case of BPNC3, the Freundlich isotherm was slightly more fitting ($R^2 = 0.993$ vs. 0.979). Based on the isothermic models, in most cases monolayer coverage is the dominant adsorption mechanism of vanadium by the bisphosphonate nanocellu-

Table 2 Comparison of first order and second order adsorption rate constant and calculated and experimental q_e values of different nanocelluloses

Nanocellulose sample	q_e (exp) (mmol/g)	First order			Second order		
		k_1	q_e (calc.) (mmol/g)	R_2	k_2	q_e (calc.) (mmol/g	R_2
BPNC1	0.18	0.00046	0.055	0.9871	0.65	0.18	0.9997
BPNC2	0.19	0.00046	0.032	0.7300	1.05	0.19	0.9998
BPNC3	0.21	−0.0025	0.024	0.8664	0.76	0.21	0.9999
BPNC4	0.20	0.030	0.0090	0.8677	−17.5	0.20	1.0000

Conditions: 0.22 mmol/l of vanadium; 1 g/l of nanocellulose; pH 3; volume of 50 ml; room temperature

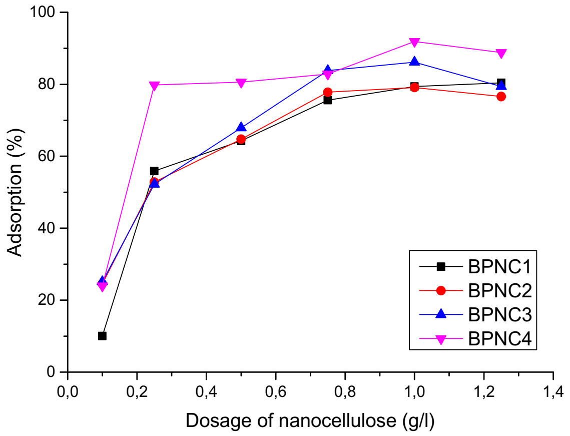

Fig. 4 Percentage of vanadium removal with respect to nanocellulose concentration. Conditions: 0.23 mmol/l of vanadium; pH 3; volume of 50 ml; room temperature, 24 h shaking time

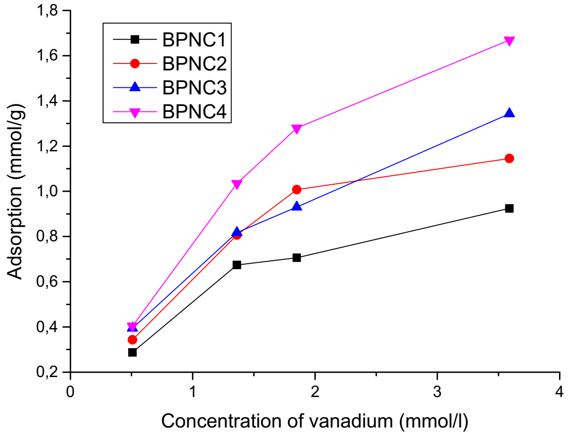

Fig. 5 Adsorption capacities of bisphosphonate nanocelluloses as a function of vanadium concentration. Conditions: 1 g/l of nanocellulose; 24 h contact time; volume of 25 ml; room temperature

loses, whereas in the case of BPNC3 heterogeneous surface sorption properties are observed. The R_L values for all bisphosphonate nanocellulose samples were between 0 and 1, indicating that the adsorption was favorable. The calculated adsorption capacity, Q_0, ranged from 1.12 mmol/g of BPNC1 to 1.98 mmol/g of BPNC4. The adsorption capacity in terms of the adsorbed vanadium per bisphosphonate group (Table 3) seemed to be constant, and thus, the increased adsorption capacity is mostly likely due to the increase in the nanocellulose bisphosphonate content. The slightly higher adsorption capacity per bisphosphonate groups of BPNC1 might be due to morphology differences as it mainly consisted of long nanofibrils, whereas other samples mostly contained short nanocrystals.

Several different biobased materials have previously been used to remove vanadium (+V) from water, but reports on the results of the adsorption of vanadium using nanocelluloses are scarce. The adsorption capacity of crosslinked chitosan (Qian et al. 2004), crosslinked chitosan functionalized with threonine (Hakim et al. 2008), and protonated chitosan flakes (Padilla-Rodríguez et al. 2015) has been reported to be 0.12, 0.93, and 0.05 mmol/g, respectively. Similar (1.93 mmol/g) adsorption capacity as observed for BPNC4 was found for Zr(IV)-impregnated collagen fibers (Liao et al. 2007), while a higher adsorption capacity was observed using a composite based on crosslinked chitosan and zirconium (4.01 mmol/g) (Zhang et al. 2014) and amine-modified poly(glycidyl methacrylate)-grafted cellulose (3.88 mmol/g) (Anirudhan et al. 2009). Inorganic nanoparticles such as octylamine functionalized magnetite nanoparticles have been reported to have a maximum adsorption capacity of 0.50 mmol/g for vanadium (Parijaee et al. 2014). The results of the

Table 3 Langmuir and Freundlich isotherm constants and ration between adsorption maximum and amount of bisphosphonate groups of nanocelluloses

Sample	q_e (exp) (mmol/g)	Langmuir				Freundlich			V adsorbed/ bisphosnate group
		Q_0	b	R_L	R^2	K_f	*n*	R^2	
BPNC1	0.92	1.13	1.69	0.54	0.9919	0.65	2.16	0.9121	6.63
BPNC2	1.15	1.34	2.57	0.22	0.9931	0.91	2.2	0.8779	6.11
BPNC3	1.34	1.58	2.11	0.2	0.9789	0.98	2.46	0.9934	5.46
BPNC4	1.67	1.98	2.92	0.09	0.9967	1.44	2.08	0.8903	6.18

Conditions: 1 g/l of nanocellulose; 24 h contact time; volume of 25 ml; room temperature current study indicate that bisphosphonate nanocelluloses have high potential to be used to remove vanadium from a water solution. The number of bisphosphonate groups can significantly enhance the adsorption capacity of nanocellulose. Thus, the reaction condition should be optimized to fully harness the potential of bisphosphonate nanocelluloses. In addition, the effect of the nanocellulose morphology on adsorption efficiency should be studied in future research.

Conclusion

Bisphosphonate nanocelluloses were observed to be efficient adsorbents for removing vanadium(V) from model water, even at a low degree of substitution. The adsorption was most efficient at low pH, indicating that adsorption is based on the complexation of vanadium by bisphosphonate nanocelluloses and the electrostatic interaction between anionic nanocelluloses and cationic vanadium species. The adsorption of vanadium followed the pseudo-second-order kinetic model, and the adsorption was mainly described by the Langmuir adsorption isotherm. The adsorption capacity correlated well with the number of bisphosphonate groups in the nanocelluloses, indicating that increasing the reaction efficiency of the chemical modification of cellulose before disintegration could further increase the adsorption capacity of bisphosphonate nanocellulose.

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