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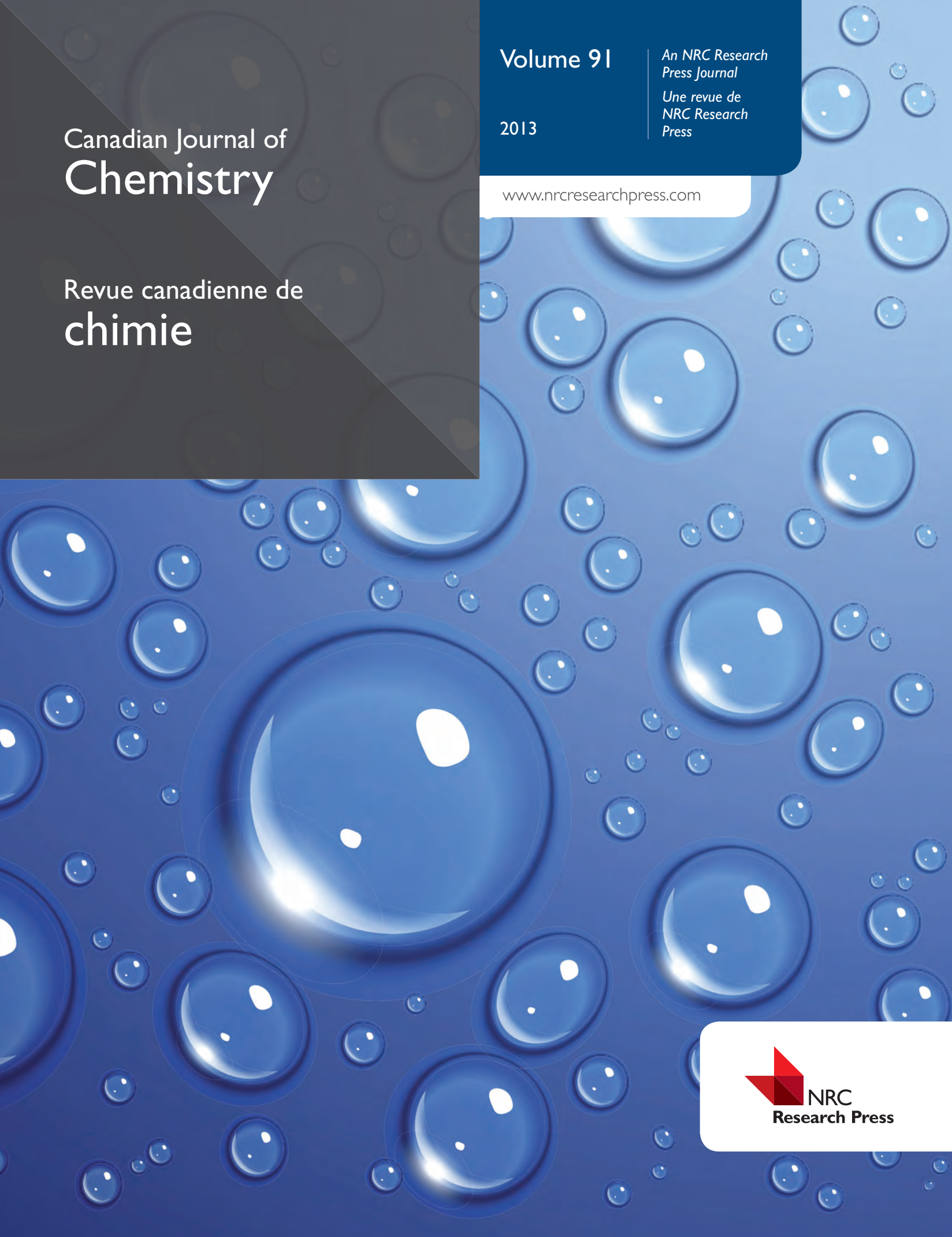

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ARTICLE

Spectroscopic studies of vanadium biosorption on different types of carbohydrate biomass

Jousy García, Juan Carlos González, María Inés Frascaroli, Silvia García, Patricia Blanes, Isabel Correia, João Costa Pessoa, and Luis F. Sala

Abstract: The biosorption potential of different types of carbohydrate biomass is investigated to evaluate their application to purify water contaminated by vanadium in environmentally relevant oxidation states (V^{IV} and V^{V}). Spectroscopic studies were done by electron paramagnetic resonance (EPR), vanadium nuclear magnetic resonance (^{51}V NMR), circular dichroism (CD), and electronic absorption in the visible range (vis). Both D-galacturonic and D-glucuronic acids are major components of plant cellular wall polysaccharides. The interaction of V^{IV} with the model ligands D-galacturonic and D-glucuronic acids showed that complexation starts at low pH values (pH 3) and that carboxylate and sugar–OH groups, as well as water molecules, are involved in the coordination. At pH > 4.5, coordination promotes the sugar–OH deprotonation and new species form with the ligand chelating the metal ion via oxygen atoms of carboxylate and of adjacent sugar–O^- donors. The studies with pectin and citric acid show the ability of both compounds to partially reduce V^{V} to V^{IV} in solution and the EPR parameters suggest coordination of carboxylate, sugar–OH, and water molecules. The interaction of V^{V} with biomass from different sources shows that grapefruit, orange peel, and plane tree fruit are the most suitable candidates for the biosorption of vanadium. Studies with V^{V} and grapefruit (or the grainless stalk of corn) indicate that the reduction takes place at the "surface" of the solid. EPR studies on the interaction of V^{IV} with different carbohydrate biomass show their ability to complex high amounts of V^{IV}. We propose that the biosorption mechanism, when the biomass is in contact with V^{V} species, involves sorption, reduction, and retention at the surface level of V^{IV} coordinated by oxygen donors of the biomass. When the interaction starts with V^{IV}, the main process just involves the uptake of the metal ion at the surface level.

Key words: vanadium, biosorption, biomass, electron paramagnetic resonance (EPR), D-glucuronic acid, D-galacturonic acid.

Résumé : On a étudié le potentiel de biosorption de divers types d'hydrates de carbones de la biomasse dans le but d'évaluer leur application dans la purification de l'eau contaminée par le vanadium dans les états d'oxydation pertinents à l'environnement (VIV et VV). Les études spectroscopiques ont été faites à l'aide de la résonance paramagnétique électronique (RPE), la résonance magnétique nucléaire du vanadium (RMN du 51V), le dichroïsme circulaire et l'absorption électronique dans la place du visible (Vis). Les acides d-galacturonique et d-glucuronique sont les composants majeurs des polysaccharides des parois des plantes cellulaires. L'interaction entre le VIV avec les ligands modèles des acides d-galacturonique et d-glucuronique a montré que la complexation commence à des valeurs basses de pH (pH, 3) et que les groupes carboxylate et OH des sucres ainsi que les molécules d'eau sont impliquées dans la coordination. À des pH supérieurs à 4,5, la coordination favorise la déprotonation du OH du sucre et la formation de nouvelles formes dans lesquelles le ligand se chélate à l'ion métallique par le biais les atomes d'oxygène du carboxylate et les O- des sucres adjacents. Les études avec de la pectine et de l'acide citrique mettent en évidence la capacité de ces deux composés à réduire partiellement le VV et VVI en solution et les paramètres de la RPE suggèrent qu'il s'effectue des coordinations au niveau des carboxylates, des OH des sucres et des molécules d'eau. L'interaction entre le VV avec la biomasse de diverses sources montre que les pamplemousses, les pelures d'orange et le fruit du platane sont les meilleurs candidats pour la biosorption du vanadium. Des études avec le VV et le pamplemousse (ou les épis de blé d'Inde sans grain) indiquent que la réduction se produit à la surface du solide. Les études RPE de l'interaction du VIV avec diverses biomasses d'hydrates de carbone montreur leur facilité à complexer de grandes quantités de VIV. Il est donc suggérer que le mécanisme de biosorption - quand la biomasse est en contact d'espèces VV - implique une sorption, une réduction et une rétention au niveau de la surface du V!V retenu par des coordinations avec des donneurs oxygène de la biomasse. Quand l'interaction commence avec le VIV, le processus principal implique seulement une insertion de l'ion métallique au niveau de la surface.

Mots-clés : vanadium, biosorption, biomasse, RPE, acide D-glucuronique, acide D-galacturonique.

Introduction

An expansion of several industrial sectors leads to an increasing demand for the usage of heavy metals. Despite an advance in pollution control techniques, heavy metals could still find their way into the environment, particularly through wastewater discharge or the leachate of solid waste. The abatement of wastewater containing heavy metals can be achieved via several techniques, such as precipitation, evaporation, etc. However, the common treatment processes have been shown to be quite expensive and ineffective for low strength wastewater.[1] Sorption (or biosorption), a process based on the passive sequestration by nonmetabolizing and nonliving biomass,[2] is the most appropriate remediation process and has been extensively employed to recover metal ions from dilute solutions. Vanadium, which is a toxic metal,

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*These authors were the main scientific guides for the experiments done in Portugal and Argentina.

has widespread industrial applications.[3–4] Moreover, both natural and anthropogenic sources and pathways yield significant vanadium emissions to the atmosphere, which are later deposited and (or) dissolved in seas, rivers, and lakes. Hence, large amounts of vanadium are discharged into the environment.[4a] The major industries contributing to water pollution by vanadium are petrochemical, ceramic, glass, textile, photography, metallurgy, and rubber. In addition, industrial production of inorganic chemicals and pigments are dominant contributors of vanadium to the atmosphere.[4b]

Although V^{V} and V^{IV} concentrations in polluted waters are usually too high for environmental disposal, they are not high enough to make their extraction possible by economically viable standard processes. Thus, it is necessary to develop alternative processes to remove vanadium ions.[2] The need for processes to remove vanadium has become a major challenge for wastewater systems. Activated carbons are unique sorbents because of their extended surface area, microporous structure, high sorption capacity, and high degree of surface reactivity. However, the high cost of activated carbon limits its large-scale use as viable and economical sorbents.

Biomass sorption is an effective and versatile method for removing heavy metals, particularly when combined with suitable biomass regeneration steps. Considerable research has been done in the search of inexpensive agricultural waste to be used as available sorbents.

The most appropriate biological biomass for sorption processes are agriculture waste or abundant seaweeds, which are both rich in polysaccharides, with low costs and no adverse effects on the environment.[2,5–9]

It is well-known that carbohydrates afford stable complexes with metal ions. Such complexes have been described as important tools in pharmacology, with carbohydrates acting as metal carriers.[10] In addition, it was shown that a polymeric structure can bind to metal ions different from its monomer structure, since a 3D polymeric structure can also bind via cross-linking and multiple binding sites.[11] Uronic acids such as D-galacturonic acid (galur), the major component of pectin natural biopolymer, is present in all plant primary cell walls.[12] These biomass fulfill the requirements of heavy metal uptake as stated previously.

The selectivity of polysaccharides from different sources for the interaction with multivalent metal ions has been reported in the literature.[2,13] Polysaccharides have been recently employed in the field of biohydrometallurgy to recover dissolved heavy metal ions from aqueous media.[14] Vanadium is a transition metal, which in its tri-, tetra-, and penta-valent oxidation states has the ability to interact with biomolecules affording stable compounds.[15] Vanadium has a preference for oxygenated environments, in which the interaction is favored when the ligand contains carboxyl and (or) hydroxyl groups[16,17] usually found in neutral and acid polysaccharides. Therefore, uronic acids (monomers and polymers) present in biopolymers such as pectins, alginic acid, and carregenans are adequate ligands for V^{IV} and play an important role in the coordination of metal ions.[18–20] The present study deals with the complexation of vanadium at different oxidation states by different biomass types, which are derived from agricultural waste and contain the polymers previously mentioned. The aim of this work is basically to determine which of the biomass under study show the highest capacity to interact with V^{V} and V^{IV}, with the purpose of being employed for remediation processes using batch and (or) column methods.

Experimental section

Materials

D-Galacturonic acid, D-glucuronic acid, pectin, citric acid, and $V^{IV}OSO_4{\cdot}4\ H_2O$ were purchased from Sigma-Aldrich and $NH_4V^{V}O_3$ from BDH. The purity of $V^{IV}OSO_4{\cdot}4\ H_2O$ was determined by analytical methods.[21] The molar mass of pectin (MW = 54 500 ± 100 g/mol) was measured by an intrinsic viscosity method.[22]

Orange peel (OP) and grapefruit (GF) were obtained from citrus, soya bean (SB) from soya, and the grainless stalk of corn (GSC) from maize; all were harvested near the city of Rosario (Argentina). Commercial GSC used in this study was "Ruby 306", a maize variety. Fruit of the plane tree (FPT) was collected from *Platanus hispanica* in the city of Rosario. These biomass samples were washed with water, dried at 40 °C for 12 h, then sieved to retain the fraction of particles in the size range of 0.3–1.2 mm (OP and GF) or 0.3–0.5 mm (SB) and stored at room temperature in sealed polyethylene bags. The GSC was powdered and washed with water, dried at 40 °C for 12 h and sieved to retain the particle size in the range of 0.12–0.5 mm. *Polysiphonia nigrescens* (PN) was collected in Cabo Corrientes (38°03′S, 57°31′W, Mar del Plata, Argentina). This biomass was washed several times with deionized water to remove extraneous particles and salts. PN was then dried at 40 °C for 24 h. The dried algae biomass was chopped, sieved, and the particles with an average size of 0.5 mm were used for sorption experiments. All the sieved biomass was stored at room temperature in sealed polyethylene bags.

Spectroscopic studies

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 400 MHz spectrometer. To the NMR samples, 5% of D_2O was added to lock the NMR experiment and the ^{51}V NMR chemical shifts were referenced relative to an external neat $VOCl_3$ sample at $\delta = 0$ ppm. The acquisition parameters were as follows: 155 KHz spectral width, 25 μs pulse width, 0.1 s acquisition time, and 50 Hz line broadening.

Visible spectra were recorded on a PerkinElmer ultraviolet (UV)–visible Lambda 35 and on a Jasco V-550 UV–vis spectrophotometer with fully thermostatized cell compartments (±0.20 °C). Circular dichroism (CD) spectra were measured on a Jasco 720 spectropolarimeter in the visible wavelength range. The electron paramagnetic resonance (EPR) spectra were obtained either on a Bruker EMXO spectrometer (room temperature spectra) or a Bruker ESP 300E spectrometer operating at X-band frequencies (~9.7 GHz). Microwave generation was by a klystron (04 ER) and frequencies were measured with a built-in frequency counter. The EPR spectra of the solutions were measured either at room temperature or at 77 K (on glasses made by freezing solutions in liquid nitrogen). To the samples measured at 77 K, 5% of ethylene glycol was added to avoid the aggregation of the molecules upon freezing. Whenever comparisons were made, the EPR acquisition parameters were kept constant for all samples, namely, the number of scans, the modulation frequency (100 kHz), modulation amplitude (4.039 G), sweep time (83.886 s), and receiver gain.

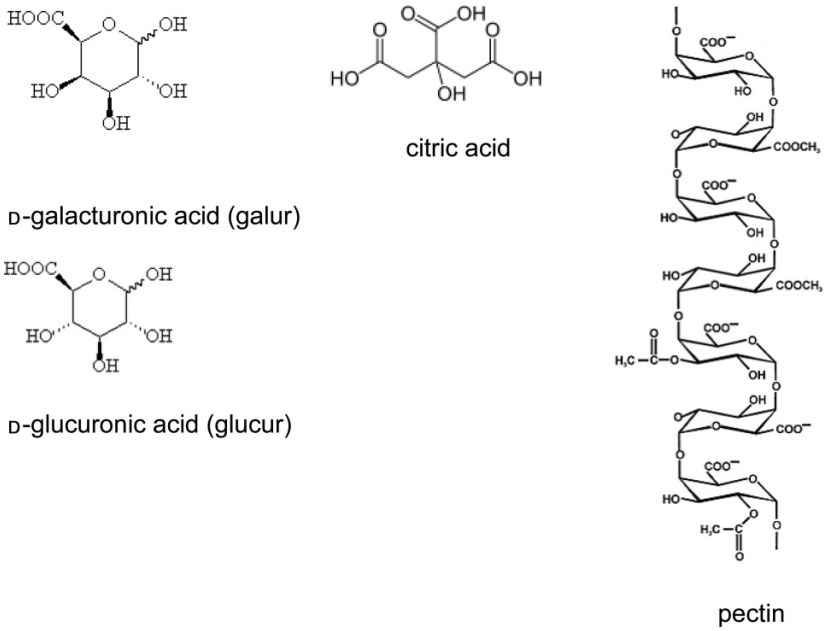
Uronic acids interaction with V^{IV}

A solution containing V^{IV} (5 mmol/L or 10 mmol/L) and D-galacturonic acid (galur) or D-glucuronic acid (glucur) (100 mmol/L) was prepared in H_2O and the pH set to 3.0 with HCl (3.0 mol/L). Its visible and CD spectra were measured and a sample was collected and frozen in liquid nitrogen to measure its EPR spectrum (at 77 K). The pH was then set to 4.0 by the addition of KOH (4.0 mol/L), and new spectra were collected. Similarly, the pH was progressively raised up to 9.1–9.5 and samples were collected at each pH value. All samples were collected under aerobic conditions, thus partial oxidation might have occurred. The concentration of the vanadium stock solution was determined spectroscopically (ε (750 nm) = 17.6 $(mol/L)^{-1}\ cm^{-1}$).

Pectin and citric acid interaction with V^{V}

5.0 g (0.092 mmol) of pectin and citric acid (0.026 mol) were dissolved independently in 200 mL of $HClO_4$ (pH 3.0). To each solution, 40 mg of $NH_4V^{V}O_3$ were added and the mixtures were stirred for 3 h. Samples were filtered and analyzed by EPR (77 K, after the addition of 5% ethylene glycol) and ^{51}V NMR (after addition of 5% D_2O). Time evolution of the Pectin–V^{V} mixtures was

Scheme 1. D-Galacturonic acid (galur), D-glucuronic acid (glucur), citric acid, and pectin structures. Each of these molecules contains several chiral centers, except citric acid, which has only one.



followed by electronic absorption in the visible range during 24 h at pH 3.0 and room temperature.

V^{V} biosorption by biomass

Experiment 1

$HClO_4$ (200 mL; pH 3.0) was added to 0.5 g of biomass (GF, GSC, or FPT) and stirred for 3 h. The biomass was filtered and 40 mg of $NH_4V^{V}O_3$ was added to the liquid part. The mixture was then gently stirred for 3 h. Samples were then taken for EPR and ^{51}V NMR measurements.

Experiment 2

$HClO_4$ (200 mL; pH 3.0) and $NH_4V^{V}O_4$ (40 mg) were added to 0.5 g of biomass (GF, GSC, or FPT). After 5 h, some samples showed a greenish color, particularly the GF essay. The samples were stirred for 24 h and aliquots of the filtered solution for EPR analysis were taken at 1, 3, 5, and 24 h. ^{51}V NMR samples were taken after 5–6 h. For the spectroscopic analysis of the solid biomass, the mixture was filtered and thoroughly washed with 200 mL of $HClO_4$ (pH 3) in small portions. After being dried under vacuum, the solid was analyzed by EPR. In the case of the FPT, the pH was set to 2.5 with $HClO_4$ and the filtered liquid sample was analyzed by ^{51}V NMR only after 24 h and by EPR at 2, 5, and 24 h.

V^{IV} biosorption by biomass

Biomass (GF, OP, PN, SB, and GSC) samples to evaluate the interaction with V^{IV} were prepared the following way: the biomass (0.5 g) was suspended in 200 mL of distilled water, the pH was adjusted to 3.0, and $V^{IV}OSO_4$ (40.0 mg) was added. The samples were stirred for 24 h and filtered, washed, and dried. The EPR of the solid samples was measured at liquid nitrogen temperature (77 K) in quartz tubes.

Results and discussion

D-Galacturonic acid (galur) and D-glucuronic acid (glucur) interaction with V^{IV}

The remediation processes known as biosorption are based on the passive sequestration by nonmetabolizing, nonliving biomass. Such biomass is a complex matrix with many types of different chemically active groups. They show some tendency to bind chemical substances or ions by attracting and incorporating them from the solution to the solid biomass.[23]

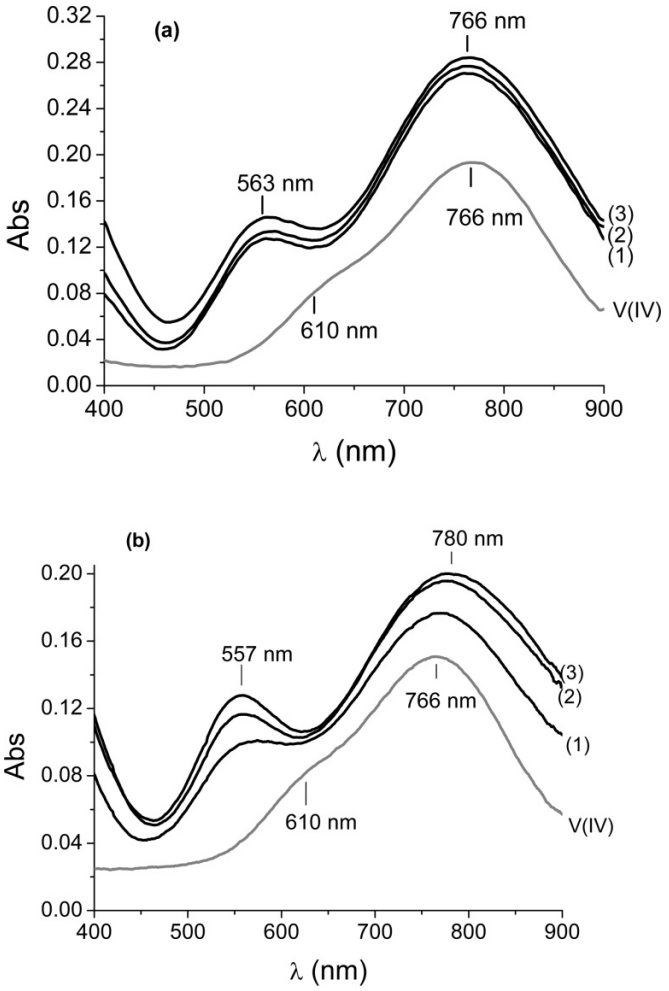
Galur and glucur (Scheme 1) are sugar molecules with terminal carboxylic groups. Since the carboxylic groups are present in carbohydrate polymers, they were therefore used as models for carbohydrate coordination. Our studies started with the assessment of the galur– and glucur–V^{IV} interactions with $V^{IV}O^{2+}$ at different pH values and metal to ligand molar ratios by several spectroscopic techniques.

Visible absorption spectra were recorded with different uronic:V^{IV} ratios at pH 4.0. The spectrum of the square pyramidal $V^{IV}OSO_4$ shows a main d–d band at 766 nm with a shoulder at ~610 nm (Fig. 1) due to transitions: $d_{xy} \rightarrow d_{xz},d_{yz}$ ($b_2 \rightarrow e_{\pi^*\ in\ C4v}$ symmetry, designated as band I) and $d_{xy} \rightarrow d_{x^2-y^2}$ ($b_2 \rightarrow b_1^*$ in C_{4v} symmetry, designated as band II), respectively.[24] After mixing the model uronic acids with $V^{IV}OSO_4$, the band at 766 nm shifts to ~780 nm (glucur–V^{IV} mixtures). The shoulder at 610 nm (band II) becomes a distinct band at 563 nm (galur–V^{IV} mixture) and 557 nm (glucur–V^{IV} mixtures). The intensity of both absorption bands increase as the concentration of uronic acid increases. These spectroscopic changes must be attributed to the coordination of donor atoms of uronic acid to V^{IV}. The pattern of the absorption spectra recorded suggests that the formed complexes adopt square pyramidal or bipyramidal geometries.[25,17]

The stability of the reaction mixtures was checked during 60–90 min in aerobic conditions and only a minimum quantity of V^{V} was produced due to the oxidation of V^{IV}. However, this process is very slow or even negligible for the higher uronic:V^{IV} ratios.

Visible spectra were also measured at several pH values for solutions containing a ligand:metal ratio of 20:1 or 10:1. They are included in the Supplementary data (Figs. SI1 and SI2). The "high" baselines are due to ligand absorption, which is present in quite a high concentration. These bands are probably due to derivatives resulting from the Maillard reaction.[26] For both $V^{IV}O$–glucur and $V^{IV}O$–galur systems, the spectra (visible absorption and circular dichroism, see the following) recorded at pH ~3 show two d–d bands, which is typical of $V^{IV}O$–complexes with a five-coordinate square-pyramidal geometry or six-coordinate bipyramidal geometry.[17] The bands are assigned as follows: band I (attributed to transitions $d_{xy} \rightarrow d_{xz},d_{yz}$) at ~760 nm and band II ($d_{xy} \rightarrow d_{x^2-y^2}$) as

Fig. 1. (*a*) Visible spectra of solutions containing $V^{IV}OSO_4$ (0.011 mol/L), grey spectrum, and galur + $V^{IV}OSO_4$ at pH 4.0. Galur:$V^{IV}O$ molar ratios: (1) 10:1, (2) 15:1, and (3) 30:1. (*b*) Visible spectra of solutions containing $V^{IV}OSO_4$ (0.009 mol/L), grey spectrum, and glucur + $V^{IV}OSO_4$ at pH 4.0. Glucur:$V^{IV}O$ molar ratios: (1) 10:1, (2) 15:1, and (3) 30:1.



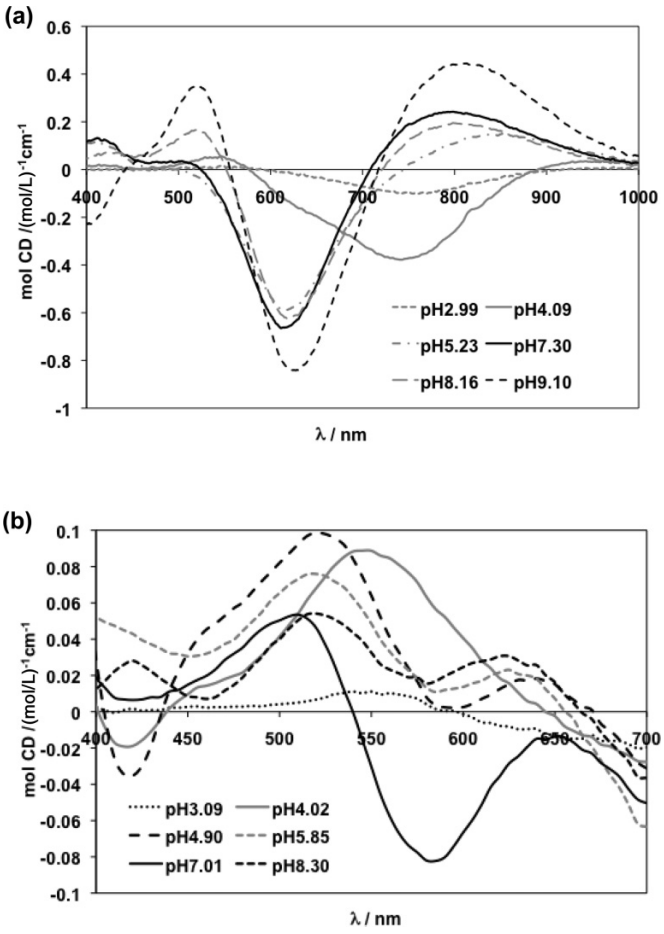
a shoulder at ~620 nm (band III ($d_{xy} \rightarrow d_{z^2}$) is masked under a strong charge transfer (CT) band with λ_{max} in the UV range). Clear evidence for complex formation at this pH value is observed since there is a shift to the higher energy of band II (when compared to the spectrum of a $V^{IV}OSO_4$ solution, see Fig. 1).

As the pH is increased, band I is split in two (particularly evident in the case of galur) due to the removal of the degeneracy of orbitals d_{xz} and d_{yz} as a consequence of the lower symmetry of the formed complexes.

For the present systems, if no derivatives from the Maillard reaction are formed in the 400–1000 nm range, only d–d bands due to the formation of $V^{IV}O$ complexes are detected. As the pH is increased, changes in the visible absorption spectra are seen and are consequences of the modification in the amount and type of the $V^{IV}O$ complexes present. However, the assignment of the changes observed for the particular $V^{IV}O$ complexes is not straightforward.

When several species are present in solution and the ligand is chiral, as only chiral species are "active" in circular dichroism (CD) measurements, this spectrophotometric technique presents several advantages. In fact, as the present chiral ligands do not absorb in the visible range, only the $V^{IV}O$-chiral species will show up in the 400–1000 nm range. Moreover, CD bands may be positive or

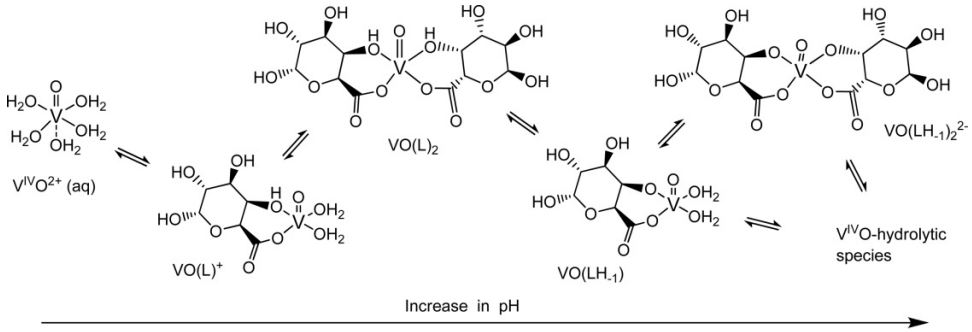
Fig. 2. CD spectra of solutions containing $V^{IV}OSO_4$ and uronic acids at several pH values indicated in the figure: (*a*) [V^{IV}] = 10 mmol/L, [galur] = 100 mmol/L; (*b*) [V^{IV}] = 5 mmol/L, [glucur] = 100 mmol/L.



negative and the signal intensity presents a much broader range than isotropic UV–vis absorption. Thus, in terms of detection and identification of distinct chiral species formed, CD is much simpler and informative to use. Thus, to get a deeper insight of the speciation of the CD systems, measurements were done.

Figure 2 shows the measured CD spectra of the same solutions. CD spectra in the visible range can only be measured if chiral ligands are coordinated to V^{IV} centers, yielding induced CD signals in the d–d bands.[27] In addition, CD is more informative than electronic absorption spectroscopy since (*i*) the CD bands can have opposite signs, being more easily observed when compared to the broad electronic absorption bands, and (*ii*) only $V^{IV}O$–uronic acid complexes have nonzero CD signals, e.g., $(V^{IV}O(OH_2)_5)^{2+}$ ($V^{IV}O^{2+}$(aq) in Scheme 2 will not contribute to the signal measured). For both $V^{IV}O$–glucur and $V^{IV}O$–galur systems, since weak CD signals appear in the visible region, it is clear that at pH 3.0 there is complex formation to some extent. These signals can only be due to the interaction of V^{IV} in $V^{IV}O$ with chiral groups of the ligands, involving the O atoms of COO^- (O_{COO-}) and sugar–OH (O_{ROH}) groups. The CD spectra measured at pH ~ 4.0 are significantly more intense than those measured at pH 3.0, and have a somewhat similar pattern of bands, although some changes in the type of signal recorded are already visible due to an increase in the amount of the V^{IV}–uronic acid complexes formed. This type of CD spectra has been observed for other vanadium complexes with ligands coordinated through carboxylate groups.[28] At pH 3–4, the galur–V^{IV} mixture (Fig. 2*a*) presents strong, negative bands at ~740 nm (band I), a weak positive band at 545 nm (band II), and a

Scheme 2. Change in the binding sets observed in aqueous solutions containing $V^{IV}O^{2+}$ and molar excess of uronic acids (the example here is for D-glucuronic acid) as the pH is increased. The formation of $V^{IV}O(LH_{-1})_2^{2-}$ is detected for pH > ~9 and corresponds to the A_z^{est} value of 154.8 × 10^{-4} cm^{-1}. For pH > 6, the relative amount of $V^{IV}O$–hydrolytic complexes, namely $((V^{IV}O)_2(OH)_5^-)_n$,[17] increases significantly.



very weak positive band centered at 414 nm (this could be band III or CT bands). At pH 5.2, different complexes form since band I is split in two (band Ia, positive and centered at 850 nm, and band Ib, negative, with a maximum at 614 nm), and band II is blue shifted to 520 nm. For pH ≫ 5, the spectra increases in intensity and some changes are observed. However, the pattern of the bands is globally maintained (not many changes are observed), except at pH 9.10 where a negative band is observed with a maximum at ~400 nm.

At pH 4, glucur–V^{IV} CD spectra afford negative bands above 700 nm (band I, not shown), a strong positive band at 545 nm (band II), and a weak negative band centered at 413 nm (probably band III), Fig. 2*b*. At pH 4.9, a different complex must be formed with lower symmetry, since band I is split in two (band Ia, negative, and band Ib, positive with a λ_{max} at 640 nm), and band II is blue shifted to 520 nm. This is the pH value that shows CD spectra with the highest intensity. At pH ~ 6, all bands are blue shifted and band III becomes positive. The spectrum measured at pH 7 is totally different. So, a new species must be formed and new changes are observed again above pH 8. Thus, we can conclude that complex formation starts at pH ~ 3. As the pH is increased, the tendency for interaction with the deprotonated hydroxo groups increases as a consequence, and several different V^{IV} species are formed.

To help with the assignment of the groups involved in the coordination at different pH values, the paramagnetic V^{IV}–uronic species were further studied by EPR spectroscopy at 77 K. In the case of $V^{IV}O$ complexes, the spin Hamiltonian parameters, g_x, g_y, g_z, A_x, A_y, A_z, from each experimental EPR spectrum may be obtained by simulation using appropriate computer programs.[29] The A_z value can be estimated (A_z^{est}) using an additivity relationship proposed by Wüthrich[30] and Pettersson et al.[31] with an estimated accuracy of ±3 × 10^{-4} cm^{-1} ($A_z^{est} = \Sigma A_{z,i}$ (i = 1–4), where the $A_{z,i}$ values are the contributions of each of the four equatorially coordinated donor groups). This value can be correlated with the type of binding groups in the equatorial position since each donor group has a specific contribution to the A_z. The relevant values for the present ligands are (in ×10^4 cm^{-1}):[29] $A_z(O_{H2O})$ = 45.65, $A_z(O_{ROH})$ = 45.65, $A_z(O_{COO-})$ = 42.1, $A_z(O_{RO-})$ = 35.32, and $A_z(O_{OH-})$ = 38.67. The sum of the contributions of the four equatorial groups gives the A_z^{est} value that may then be compared with the A_z observed for each equatorial binding set considered.[32]

Figure 3 shows some of the spectra recorded and Table 1 collects the spin Hamiltonian parameters obtained by simulation. Most spectra show axial symmetry.

From the observation of Figs. 1–3 and by comparison with the spin Hamiltonian parameters obtained (included in theTable 1), we can conclude that there is complex formation at pH ~ 3. At this pH value, only the carboxylate group may be deprotonated (pK_{glucur} 2.98 and pK_{galur} 3.19).[33] Depending on the ligand to metal molar ratios (L:M ratios), either one or two ligand molecules coordinate to $V^{IV}O^{2+}$ through the COO^- groups; the O atoms of the protonated sugar–OH groups (O_{ROH}) of the ligand may also coordinate to V^{IV} (see Scheme 2). We cannot distinguish the O_{H2O} from the O_{ROH} bound to V^{IV} by EPR alone, but the CD intensity increases as more sugar–OH groups bind to V^{IV}. Thus, the main V^{IV} species present probably involves square pyramidal complexes with binding sets, (O_{COO-}, O_{ROH}, 2 × O_{H2O})$_{equatorial}$ and (2 × O_{COO-}, 2 × O_{ROH})$_{equatorial}$, corresponding to $V^{IV}O(L)^+$ and $V^{IV}O(L)_2$ species, respectively (Scheme 2); their relative amount depending on the pH and L:M ratios. Therefore, the A_z^{est} values calculated for these binding sets are in agreement with those found experimentally, with $V^{IV}O(L)_2$ increasing in concentration as pH and L:M ratios increase.

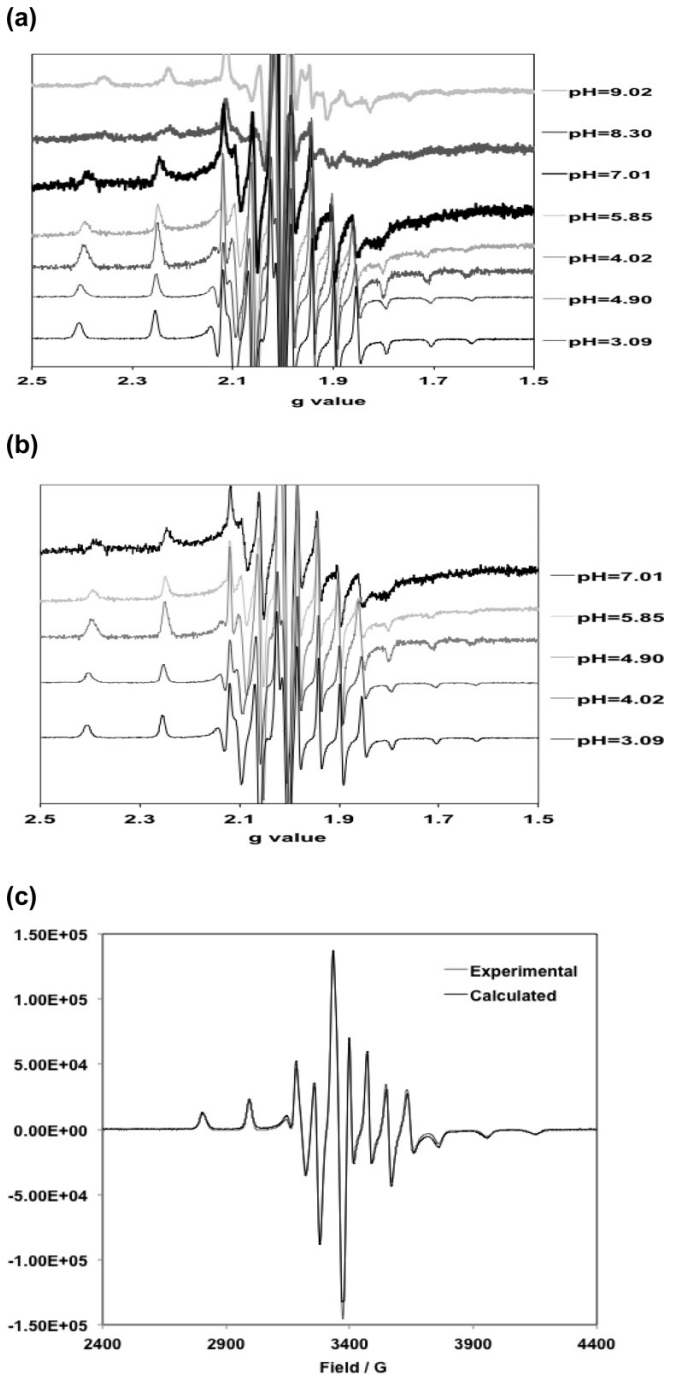
At pH 4, there is a slight decrease in the A_z values due to the formation of a higher relative amount of $V^{IV}O(L)_2$ species. This is also corroborated by the CD spectra. Thus, at pH 4, there is a significant coordination of the ligand to the $V^{IV}O$ center and the binding set is predominantly (2 × O_{COO-}, 2 × O_{ROH})$_{equatorial}$.

Since the solutions used for EPR measurements in the $V^{IV}O$–glucur system have higher L:M ratios (L:M = 20:1) than in those of the $V^{IV}O$–galur system (L:M = 10:1), the A_z values measured in the former system are lower and both values are closer to those expected for $V^{IV}O(L)_2$ species. Similar trends were previously found for $V^{IV}O$–amino acid $V^{IV}O$–dipeptide systems.[28a,34] As the pH is increased to 5–6 and the metal ion coordination promotes the sugar–OH deprotonation and coordination, new species form and the ligands can chelate the metal ion via O_{COO-} and the adjacent O_{RO-}. The A_z values obtained suggest a binding mode involving carboxylate, RO^- groups, and two water molecules in an equatorial binding mode: (O_{COO-}, O_{RO-}, 2 × O_{H2O})$_{equatorial}$,[17,29] complex $VO(LH_{-1})$ in Scheme 2. The coordination of two uronic ligands with this binding mode, i.e., (2 × O_{COO-}, 2 × O_{RO-})$_{equatorial}$, would yield an A_z^{est} value of ~155 × 10^{-4} cm^{-1}, with this being very far from the observed values of ~169–170 × 10^{-4} cm^{-1}. Thus, the proposed binding modes at pH 5 and 6 are those indicated in Table 1. The lower symmetry of this species, when compared to the species present at pH 3–4, is corroborated by the splitting of band I into two bands with opposite signs in the CD spectra. The visible absorption spectra also display the splitting of band I (see Figs. SI1 and SI2 in the Supplementary data).

At pH values above 6, the EPR spectra of V^{IV}–glucur complexes lose intensity due to partial oxidation and (or) formation of V^{IV} hydrolytic and (or) oligomeric species. The A_z values continue to decrease and the EPR spectra give lower signal to noise ratios, therefore the simulations are not so reliable as for lower pH values. However, it was possible to calculate the spin Hamiltonian parameters for the V^{IV}–galur system at pH = 10 where two distinct species are present (seeTable 1), which correspond to $VO(LH_{-1})$ and $VO(L)_2$ complexes.

The spectroscopic data obtained from the evaluation of the binding of these uronic acids to $V^{IV}O^{2+}$ suggest that biomass containing carbohydrate polymers may be suitable for the uptake of

Fig. 3. First derivative EPR spectra of frozen solutions (at 77 K) containing $V^{IV}OSO_4$ and uronic acids at several pH values: (*a*) [V^{IV}] = 10 mmol/L, [galur] = 100 mmol/L; (*b*) [V^{IV}] = 5 mmol/L, [glucur] = 100 mmol/L; (*c*) Experimental and calculated spectra measured for the galacturonic acid–vanadium system. [V^{IV}] = 10 mmol/L, [galur] = 100 mmol/L, pH = 4.90.



$V^{IV}O^{2+}$ from aqueous solution in a wide pH range. This statement is supported by the ability of sugars to bind VO^{2+} ions with high constant stability around 8.0×10^3 at 25 °C (μ = 0.100 mol/L). The last value was already determined in a previous study.[35]

Vanadium (V) interaction with pectin and citric acid

V^{IV} and V^{V} may find their way into the natural environment in particular surface waters as toxic pollutants. V^{IV} can be taken up by a variety of ligands such as carboxylic acids and pectin, which are present in biopolymers.

Since vanadium is found in the +5 oxidation state in wastewaters, we evaluated the ability of pectin (present in some types of biomass) and citric acid (a natural reducing agent) to reduce and bind V^{V} and V^{IV}. Two solutions were prepared at pH 3 with both ligands and V^{V}; Fig. 4 shows the EPR spectra of the samples measured under similar conditions (gain, modulation amplitude, and number of accumulations). The spectra were simulated and the parameters are included inTable 2.

The spectra depicted in Fig. 4 clearly indicate that a significant amount of V^{V} was reduced to V^{IV}. Taking into account the additive rule mentioned previously and the contribution of each possible donor, the obtained A_z^{est} values indicate the binding of one O_{COO-} and three O_{H2O} donors, which in terms of EPR parameters are equivalent to O_{ROH} donors[31] (O_{H2O} and O_{ROH} donors are not distinguishable by EPR). Despite the existence of too many qualifiers, the binding probably involves only O_{COO-} and O_{ROH} donors, both of which are present in pectin and citrate compounds.

The ^{51}V NMR experiments with the same solutions show the presence of only V_{10} species (decavanadates) in the case of pectin (peaks at −420, −502, and −521 ppm), indicating that pectin is unable to complex V^{V} at this pH. For the citric acid sample, the ^{51}V NMR spectrum is much less intense and three peaks are observed at −512, −540, and −545 (shoulder) ppm. The formation of mono-, di-, and tri-nuclear vanadate complexes are known for citric acid and related α-hydroxycarboxilic acids due to the ability of the alkoxy oxygen to participate in binding to two V^{V} centres.[36] We tentatively assign the peaks to the following species: VL^{2-}, $V_2L_2^{2-}$, and $V_3L_2^{3-}$. We can conclude that citric acid is able to reduce vanadium and coordinate it in both oxidation states. Pectin has a lower reducing power, however it can bind vanadium in the +4 oxidation state.

Interaction of V^{IV} and V^{V} with biomass

To determine the sorption ability of different types of biomass, the interaction with V^{IV} and V^{V} was evaluated by EPR and ^{51}V NMR. We used biomass from different sources: pectic biomass: OP, GF; algae biomass: PN; and lignocellulosic biomass: GSC, SB, and FPT.

The changes in the EPR and ^{51}V NMR spectra were evaluated over a period of 24 h for samples containing 0.5 g of biomass and V^{V} (40 mg of NH_4VO_3) at pH 2.8. Figure 5 shows the EPR spectra collected after 24 h (measured with the same acquisition parameters) for the liquid that was in contact with the different biomass samples.

Although quite extreme acquisition parameters were employed (high receiver gain, modulation amplitude, etc.), a very weak EPR signal was observed for samples with SB, PN, and the GSC after 24 h only. Consequently, we can state that the amount of $V^{IV}O^{2+}$ formed by a redox reaction is negligible, and these biomass samples do not have the ability to reduce V^{V} to V^{IV} in these experimental conditions. In contrast, for the GF and OP samples clear EPR signals are observed, as shown in Fig. 5. For both liquid samples after 1 h, V^{IV} is already present (see the spectra included in Figs. SI3-1 and SI3-2 in the Supplementary data). There is a slight increase after 5 h and an even further increase after 25 h. Thus, we can conclude that GP and OP are very promising in their ability to reduce V^{V} to V^{IV}. The obtained results may be the consequence of the different composition of the biomass employed in the present study as appreciated in Table SI1 found in the Supplementary data. The higher percentage of pectin, plus citric acid in OP and GP, explains the high reactivity of this type of biomass[37a] with V^{V}, as well as the retention of V^{IV}. PN is a red seaweed and therefore a different type of biomass without pectin in its composition. The red algae are characterized by the presence of other polysaccharides like carrageenan, which contains a number of different linear sulfated galactans. Sulfonic groups on the biopolymer are

Table 1. Spin Hamiltonian parameters obtained by simulation of the EPR spectra[29] of uronic acids–V^{IV} aqueous solutions (using an excess of uronic acid).

pH	g_x, g_y	g_z	A_x, A_y ($\times 10^4$ cm^{-1})	A_z ($\times 10^4$ cm^{-1})	Equatorial binding set	A_z^{est} ($\times 10^4$ cm^{-1})
D-Galacturonic acid (100 mmol/L) + $V^{IV}OSO_4$ (10.0 mmol/L)						
$V^{IV}O(H_2O)_5^{2+}$	1.980	1.933	68.2	182.6	$4 \times O_{H2O}$	182.8
2.99	1.978	1.938	64.3	176.7	O_{COO-}, O_{ROH}, $2 \times O_{H2O}$	179.0
					$2 \times O_{COO-}$, $2 \times O_{ROH}$	175.5
4.09	1.977	1.940	61.9	173.8	$2 \times O_{COO-}$, $2 \times O_{ROH}$	175.5
5.23	1.977	1.944	58.0	168.9	O_{COO-}, O_{RO-}, $2 \times O_{H2O}$	168.7
9.10	1.977	1.944	58.0	167.9	O_{COO-}, O_{RO-}, $2 \times O_{H2O}$	168.7
	1.979	1.953	51.3	155.1	$2 \times O_{COO-}$, $2 \times O_{RO-}$	154.8
D-Glucuronic acid (100 mmol/L) + $V^{IV}OSO_4$ (5.0 mmol/L)						
$V^{IV}O(H_2O)_5^{2+}$	1.980	1.933	68.2	182.6	$4 \times O_{H2O}$	182.6
3.09	1.977	1.940	63.0	174.6	$2 \times O_{COO-}$, $2 \times O_{ROH}$	175.5
4.02	1.968	1.940	61.7	173.4	$2 \times O_{COO-}$, $2 \times O_{ROH}$	175.5
4.90	1.976	1.943	59.1	170.4	O_{COO-}, O_{RO-}, $2 \times O_{H2O}$	168.7
5.85	1.977	1.944	58.1	169.0	O_{COO-}, O_{RO-}, $2 \times O_{H2O}$	168.7

Fig. 4. First derivative EPR spectra measured at 77 K for the pectin and citric acid samples after contact for 3 h with a solution containing $NH_4V^VO_3$ at pH 3 and room temperature.

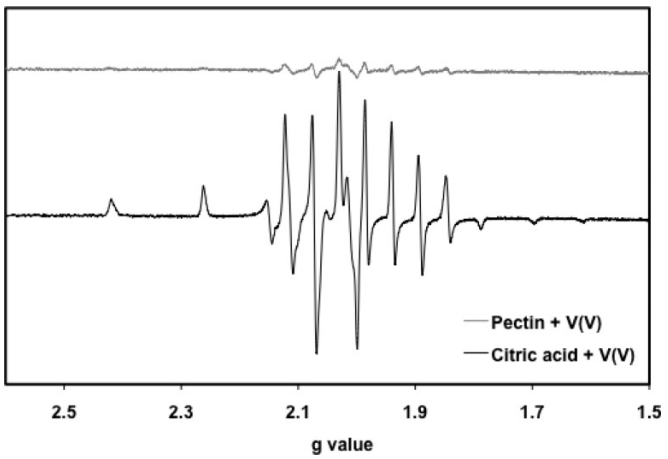


Table 2. Spin Hamiltonian parameters obtained by simulation of the spectra of Fig. 4.

Compound	g_x, g_y	g_z	A_x, A_y ($\times 10^4$ cm^{-1})	A_z ($\times 10^4$ cm^{-1})
Citric acid	1.978	1.937	67.6	179
Pectin	1.978	1.937	67.5	180

responsible for metal binding.[37b] Since the intensity of the spectra is not high enough for spectral simulation, we cannot propose which binding groups are used in the V^{IV} coordination. However, considering the previous results regarding the pectin and uronic acids capacity to coordinate V^{IV} and the EPR results, we can propose that pectin is involved in the coordination, probably through O_{COO-} and O_{ROH} donors, since this polysaccharide is present in these biomass samples in considerable amounts (~9% for GF).

In the case of the FPT, which is shown in Fig. 6, the reduction of V^V to V^{IV} was quite effective. The spectra of the liquid sample (see 2, 5, and 24 h in Fig. 6) were simulated and spin Hamiltonian parameters were obtained: $g_\perp = 1.976$, $g_\parallel = 1.935$, $A_\perp = 67.5 \times 10^{-4}$ cm^{-1}, and $A_\parallel = 180.1 \times 10^{-4}$ cm^{-1}. These parameters suggest a binding mode involving $(O_{COO-}, O_{ROH}, 2 \times O_{H2O})_{equatorial}$ for which $A_z^{est} = 179.0 \times 10^{-4}$ cm^{-1}. For the isolated solid sample, the parameters are slightly different: $g_\perp = 1.977$, $g_\parallel = 1.936$, $A_{\perp = 65.1 \times 10^{-4}}$ cm^{-1}, and $A_\parallel = 176.5 \times 10^{-4}$ cm^{-1}, and we thus propose that each $V^{IV}O^{2+}$ is bound

Fig. 5. First derivative EPR spectra measured for the frozen liquid samples (at 77 K) after contact for 24 h with a $NH_4V^VO_3$ solution with biomass at pH = 2.8. GF = grapefruit, OP = orange peel, PN = *Polysiphonia nigrescens*, GSC = grainless stalk of corn, SB = soya bean.

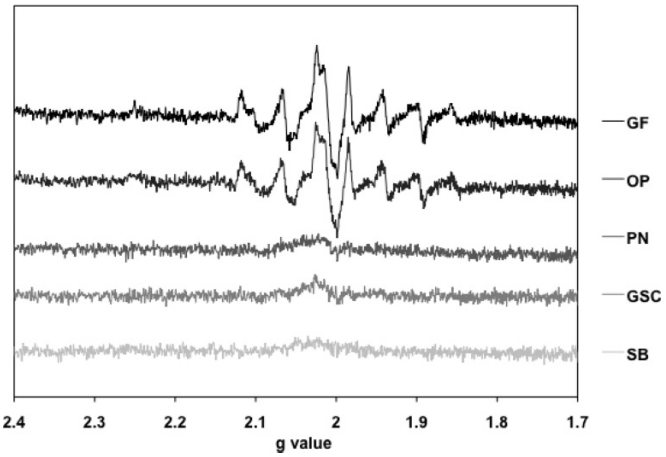


Fig. 6. Time evolution of the first derivative EPR spectra (measured at 77 K) of liquid samples collected at 2, 5, and 24 h for mixtures of $NH_4V^VO_3$ and the fruit of the plane tree biomass at pH = 2.5. The spectrum for the solid sample obtained after 24 h is also included.

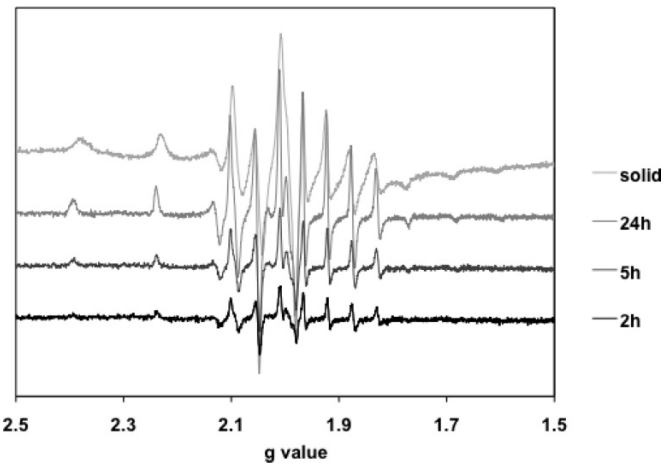


Table 3. Summary of ^{51}V NMR data for the filtrates of the biomass mixtures and $NH_4V^VO_3$ after a 5 h contact at room temperature.

Sample	pH (final)	δ (ppm; assignment)[a]	δ (ppm; assignment)[a]	δ (ppm; see the text)
GSC	3.52	–418, –497, –514 (V_{10})	–556 (V_1)	
GF	3.84	–422, –496, –512 (V_{10})	–554 (V_1)	–530, –533, –541
SB	4.55	–420, –494, –511 (V_{10})	–554 (V_1)	–536, –544
OP	4.05	–418, –497, –512 (V_{10})	–555 (V_1)	–530, –532, –542
PN	6.30	–420, –494, –510 (V_{10})	–555 (V_1), –567 (V_2?), –573 (V_4?)	
FPT	2.34	—	—	–539[b]

[a]V_{10} (decavanadates), V_4 (tetravanadates), V_2 (divanadate), V_1 ($V^VO_2^+$).[31] The V_{10} always shows three resonances due to the three different vanadate environments in the oligomeric species.[31]

[b]The spectrum was measured after 24 h.

on the biomass "surface" essentially by two O_{COO-} and two O_{ROH} groups (A_z^{est} = 175.5 × 10^{-4} cm^{-1}; see the solid sample in Fig. 6).

Upon the addition of the ammonium vanadate to the FPT sample during the ^{51}V NMR experiments, the solution turned yellow due to the formation of the colored decavanadate oligomers. However, when dissolving $NH_4V^VO_3$ other V^V species may form. The hydrolytic equilibria of V^V are often slow and other V^V-containing species are clearly identified.[31] Most spectra of the filtrate mixture samples show the presence of V_{10} (decavanadates) and V_1 ($V^VO_2^+$ at pH 2.8, 5 h). For the GF, OP, and SB filtrate mixture samples other resonances were found, which cannot be easily assigned and probably belong to complexes with biomass. The δ values are in the –530 to –544 ppm range (see Table 3), which are compatible with the formation of VO_2^+ complexes with O_{COO-} and two O_{ROH} donors. However, their amount is less than 10%. With the FTP biomass, the spectrum of the filtrate mixture sample, measured after 24 h, shows the presence of only one resonance at –539 ppm, which we assign to an octahedral complex between the soluble components of the biomass and V^V, which is in agreement with previous findings that octahedral vanadate complexes with diols[38] and hydroxy acids[39] display ^{51}V NMR shifts in the range of –535 to –545 ppm.[40]

Table 3 summarizes the data and Fig. 7 shows ^{51}V NMR spectra of the filtrate mixture samples, which were in contact with different biomass samples for 5 h (or 24 h in the case of the fruit of the plane tree). In Fig. 7, V1 is $V^VO_2^+$ (at pH 2.8) and V10, V10′, and V10″ are the resonances attributed to the three different types of V atoms in the decavanadate anion species. C represents the unassigned peaks that probably belong to complexes between V^V and the soluble components of the biomass. The δ values are compatible with VO_2^+ complexes with O_{COO-} and O_{ROH} donors. A spectrum for NH_4VO_3, which was not in contact with any biomass, is included for comparison.

Thus, we can conclude that for the majority of biomass samples, after 5 h, most of the vanadium remains in the +5 oxidation state and that most of the V^V-containing species in solution are of an inorganic nature. A few nonidentified V^V species might belong to complexes with soluble compounds released by the biomass into the solution, but judging from the intensity of the corresponding V^V signals they are present in a low amount. With the FTP sample, significant and effective reduction occurs and after 24 h most of the vanadium is in the +4 oxidation state in solution or on the surface of the biomass. A small fraction is bound to soluble biomass components in the +5 oxidation state.

To evaluate if the solid biomass is indeed able to retain the vanadium in the +4 oxidation state, biomass samples were treated with a $V^{IV}OSO_4$ solution, washed, dried, and their EPR spectra were measured at 77 K. Figure 8 shows the measured EPR spectra for the solid samples.

Very intense EPR spectra were obtained, except for the GSC. Moreover, since the spectra are similar for all samples (superimposable), all of them appear to correspond to the same vanadium coordination environment. The spectra were simulated[29] and the spin Hamiltonian parameters obtained are n, g_y = 1.978, g_z = 1.937, A_x, A_y = 65.7 × 10^{-4} cm^{-1}, and A_z = 177.9 × 10^{-4} cm^{-1}. These parameters are basically identical to those obtained for the interaction of V^{IV} with glucur and galur at low pH values (3–4), therefore we propose the binding of $V^{IV}O^{2+}$ with two O_{COO-} and two O_{ROH} donors equatorially coordinated.

Fig. 7. ^{51}V NMR spectra of the filtrate mixture samples, which were in contact with different biomass samples. A spectrum for NH_4VO_3, which was not in contact with any biomass, is included for comparison.

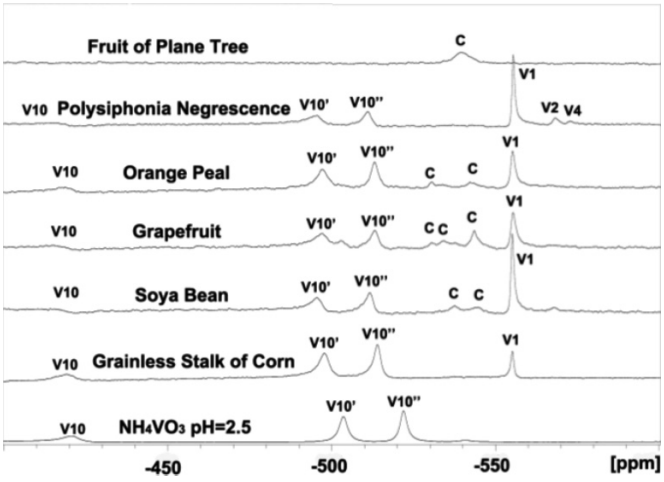


Fig. 8. Comparison of the first derivative EPR spectra of solid samples of the specified biomass treated with $V^{IV}OSO_4$ solutions. The spectra were measured at liquid nitrogen temperature (77 K). The samples were washed with water until the absence of vanadium in the filtrate.

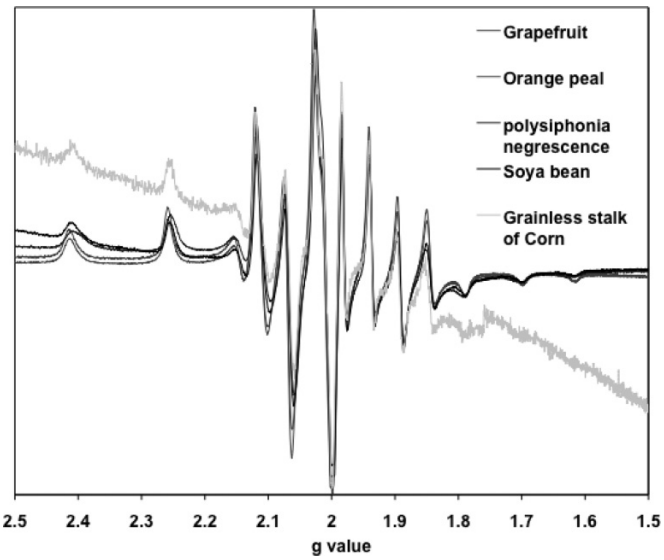
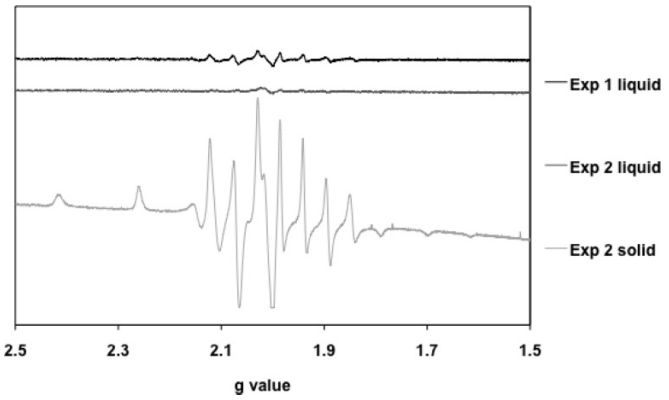


Fig. 9. First derivative EPR spectra at 77 K. For the EPR measurements, all samples were measured at 77 K under the same instrument conditions (modulation amplitude, gain, and number of scans) for comparison. See text the for details.



Thus, the experimental data show that several carbohydrate biopolymers (GF, OP, and FPT) indicate a high ability to reduce V^{V} to V^{IV} and sequester it from solution.

Vanadium(V) interaction – The influence of soluble compounds from pectic biomass

Two experiments were carried out to establish whether V^{V} interaction takes place with the biomass and (or) with the soluble compounds released to the solution by the biomass. Biomass with a high content of pectin, as GF, was used.

In Experiment 1, V^{V} was added to an acidic solution, which had been in contact with the GF biomass for 3 h (the addition of V^{V} to the filtrate was done after separation of the biomass by filtration). After 3 h of mixing, the EPR spectrum was measured and Fig. 9 (Exp 1 liquid) shows that the intensity of the spectrum is very low, suggesting a low level of reduction in solution. The EPR parameters obtained by simulation were g_x, $g_y = 1.978$, $g_z = 1.937$, A_x, $A_y = 66.7 \times 10^{-4}$ cm^{-1}, and $A_z = 178.8 \times 10^{-4}$ cm^{-1}, which are compatible with the formation of mainly $VO(L)^{+}$ complexes (see Scheme 2).

In Experiment 2, V^{V} was in contact with the biomass during the whole experiment. After filtration, the solid was washed with dilute $HClO_4$ and vacuum dried. The solid and the solution samples were analyzed by EPR.

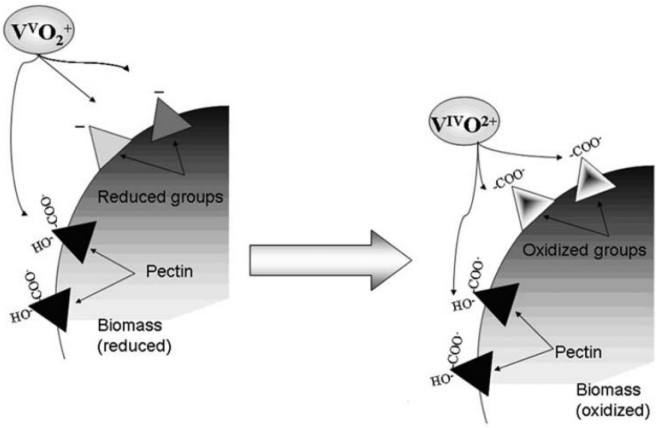
The EPR parameters obtained by simulation of the spectrum of the solid sample (see Fig. 9, Exp 2 solid) were $g_{\perp} = 1.979$, $g_{\parallel} = 1.939$, $A_{\perp} = 66.2 \times 10^{-4}$ cm^{-1}, and $A_{\parallel} = 177.9 \times 10^{-4}$ cm^{-1}, and the signal intensity was quite high. These parameters are essentially identical to those obtained in Experiment 1 (see Fig. 9, Exp 1 liquid) and they agree with the binding of $V^{IV}O^{2+}$ with two O_{COO-} and two O_{ROH} donors coordinated equatorially.

It should be noted that even though the intensities of the EPR signals in liquid and solid samples cannot be compared directly, it seems quite clear that most of the reduction takes place at the surface of the solid. Similar results were obtained in mixtures of GSC–V^{V} (the data is included in Fig. SI4 of the Supplementary data). Considering the very low level of reduction in solution, the change in intensity of EPR with time was not evaluated. Moreover, these EPR measurements are always semiquantitative.

Therefore, we can conclude that even if some reduction occurs in solution due to soluble compounds, most of this process takes place at the surface of the biomass, and the V^{IV} formed remains partially adsorbed over and absorbed in the biomass.

One of the goals of this work is finding biomaterials capable of removing vanadium from polluted aqueous solutions. It is really clear that biomass with a higher content of pectin (GP and OP) and a FPT biomass (lignocellulosic) can more effectively reduce V^{V} to V^{IV}. From an environmental point of view, the reduction step is quite important. The high capacity of pectin to bind V^{IV} makes it possible to eliminate almost the whole of the vanadium present in wastewater if the experimental conditions (pH, amount of biomass, etc.) are optimal.

Scheme 3. Proposed mechanism of V^{V-IV}–biomass interaction at pH 3.



From the EPR spectroscopic data, the uptake of V^{IV} by these biomass is evident, which indicates the presence of adsorbed V^{IV} on the biomass surface. The intensity of these signals increases with contact time, therefore the vanadium removal by biomass occurs via an adsorption-coupled reduction mechanism just as was already observed for a number of biomaterials.[37b,41] Spectroscopic data suggest a sorption mechanism by coordination involving COO^{-} and OH groups, which probably belong to pectin. In fact, columns filled with OP pectic biomass (packing density = 136 kg/m^3) are able to thoroughly purify 60 mL of a V^{IV} solution ($[V^{IV}]$ = 100 mg/L) at pH 3 and a 1.3 mL/min flow rate. Batch studies showed that the V^{IV} constant equilibrium sorption of OP, calculated from the Langmuir isotherm, was 0.1251 L/mg ($R^2 = 0.9995$). The Dubinin–Radusshkevich model was used to calculate desorption energy yielding $E = 9.8$ kJ/mol ($R^2 = 0.99217$). Batch studies also showed that 1 g of OP or GSC was able to take up 6 or 1.5 mg, respectively, of V^{IV} from the V^{IV} solution at pH 4, which represents about 30%–7.5% of the total vanadium.[42] Biomaterials showing higher interaction capacity with V^{V} or V^{IV} could be employed in sorption processes of polluted waters through batch and (or) column methods. Optimal sorption conditions studies for vanadium uptake (pH, biomass amount, flow, etc.) using factorial design experiments are still in progress.[42]

Conclusions

The studies with galur and glucur acting as uronic acid models showed the good affinity of vanadium(IV) to complex the ligand at pH values as low as 3. Different species are formed depending on pH and the deprotonation of the donor groups. At pH 3–4, the spectroscopic data indicates coordination to the metal ion through the oxygen atoms of COO^{-} and sugar–OH donors. As the pH is increased, the progressive deprotonation of the OH groups of the uronic acid molecules and coordination of the O_{RO-} donors are clearly shown. Pectin, a polymeric form of galur, shows some ability to reduce V^{V} to V^{IV} and also a certain capacity to coordinate $V^{IV}O^{2+}$ involving similar binding sets.

Considering the spectroscopic data obtained with the $V^{IV}O$–biomass systems tested, we can state that the biosorption mechanism is sorption, reduction, and retention at the surface level of $V^{IV}O$ species. The binding of $V^{IV}O^{2+}$ to the biomass systems was also confirmed.

These results highlight the utility of this type of readily available and economical biomass in remediation processes for vanadium removal from polluted waters. The studies with biomass samples showed that GP, OP, and the FTP are able to reduce V^{V},

but the other biomass sources tested here are not suitable for this purpose. Scheme 3 summarizes the hypothesized mechanism. These biomaterials could be employed in sorption processes of vanadium polluted waters once optimal conditions for vanadium uptake are determined.

Supplementary data

Supplementary data are available with the article through the journal Web site at http://nrcresearchpress.com/doi/suppl/10.1139/cjc-2012-0208.

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