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J. Guzmán, I. Saucedo, R. Navarro, J. Revilla, Guibal Eric. Vanadium Interactions with Chitosan: Influence of Polymer Protonation and Metal Speciation. *Langmuir*, 2002, 18 (5), pp.1567-1573. <10.1021/la010802n>. <hal-04664946>

**HAL Id: hal-04664946**

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Submitted on 20 Aug 2024

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# Vanadium Interactions with Chitosan: Influence of Polymer Protonation and Metal Speciation

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Chitosan is very efficient at removing vanadium from dilute solutions: sorption capacity can reach 400–450 mg V g<sup>-1</sup> under optimum experimental conditions, which correspond to pH 3. In acidic solutions, the chitosan's amine groups are protonated, and vanadate anions can be exchanged with counterions bound to -NH<sub>3</sub><sup>+</sup> sites. A correlation is observed between the speciation diagram and the sorption isotherms, and it appears that decavanadate species are more favorable to sorption than other anionic vanadate species. Selecting experimental conditions under which decavanadate ions are the predominant form of vanadium results in enhanced sorption capacities and improved sorption kinetics. The results obtained in the study of vanadate desorption confirm the high affinity of chitosan for these polyoxoanions.

## Introduction

Vanadium is frequently found in phosphorus ores.<sup>1</sup> The production of phosphoric acid using these minerals results in the extraction of large amounts of vanadate ions, which make the acid unsuitable for use in food processing. Vanadium is also present in significant concentrations in fuel oil,<sup>2</sup> its combustion in thermal power plants leads to the production of toxic fly ash. These wastes cannot be disposed of directly into the environment since vanadate can be easily leached by rainwater.<sup>3</sup> Though concentrations are too high for environmental disposal, they are not high enough to make their extraction by standard processes (solvent extraction, ion-exchange resins) economically viable. It is thus necessary to develop alternative processes for the treatment of dilute solutions. Biosorption has been studied in recent decades and microorganisms have been widely investigated for their potential to recover ions from dilute solutions.<sup>4</sup> Recently, interest has been focused on materials of biological origin: namely, byproducts from agriculture,<sup>5</sup> biopolymers.<sup>6–10</sup>

Chitosan is an amino-polysaccharide extracted from crustacean shells, it is characterized by a high affinity for heavy metals. Metal ion sorption may proceed through different mechanisms: metal cations are adsorbed through a chelation mechanism,<sup>11</sup> while metal anions can be removed by ion exchange reactions. In acidic solutions, metal anions can be exchanged with the counteranions on the protonated amine sites.<sup>12–16</sup> Despite the abundant literature on metal ion sorption using chitosan, few investigations have focused on the interaction mechanism, and these studies are mostly dedicated to the macroscopic characterization of sorption performance. The importance of metal speciation has been underestimated. Recently, Guibal et al.<sup>16</sup> have shown that molybdate sorption on chitosan derivatives is controlled by the predominance of polynuclear species. The understanding of interaction mechanisms and the identification of adsorbable species facilitate the optimization of the process: the pH can be selected taking into account the protonation properties of chitosan, and the metal speciation. The influence of metal speciation has been cited for the biosorption of precious metals.<sup>15,17</sup> Piron and Domard<sup>18</sup> discussed the influence of the speciation of uranium, in the form of hydrolyzed species and in the presence of carbonate, on its sorption by chitosan. Lasko and Hurts<sup>19</sup> investigated the influence of silver speciation in the presence of anionic chelating agents on metal removal using chitosan. They correlated

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the sorption performance and mechanism to pH and metal speciation. The influence of metal speciation on the interactions of chitosan with metal ions has also been briefly discussed by Draget et al.<sup>20</sup> to describe the gelation of chitosan in the presence of molybdate ions.

This work focuses on the study of vanadate sorption by chitosan. Sorption isotherms were performed at different pHs, at which different vanadate species predominate. Sorption isotherms were compared to the speciation diagram in order to correlate the relative concentration of selected species with the shape of the isotherm. Complementary experiments were performed on sorption kinetics under different experimental conditions, varying the pH and the metal concentration, to check the influence of metal speciation on sorption rates. Finally, desorption was performed under controlled conditions to check the reversibility in the sorption process: desorption yield from a loaded sorbent was measured at different pHs.

### Materials and Methods

**Materials.** Chitosan flakes were supplied by Aber-Technologie (Brest, France). Flakes were characterized by their deacetylation degree at 87% and their molecular weight at ca. 125,000. Samples were ground and sieved to 0–125  $\mu\text{m}$ . Chitosan was used without cross-linking since this treatment may involve a reduction in the number of free amine groups. The dissolving of chitosan at low pH was avoided using sulfuric acid for pH control. Indeed, in sulfuric acid solutions chitosan is stable. Ammonium vanadate was supplied by Fluka (Switzerland), and sulfuric acid and sodium hydroxide were purchased from Carlo Erba (Italy).

**Sorption Procedure.** Preliminary experiments on the study of the influence of pH on V(V) sorption were performed by mixing 100 mg of chitosan with 200 mL at the concentration of 200 mg V L<sup>-1</sup>, with controlled pH (between pH 1 and pH 8 in unit steps of 0.5 pH). Experiments were performed at 20  $\pm$  1 °C. The solutions were agitated using a reciprocal shaker for 72 h (the contact time necessary for reaching equilibrium). Samples were then withdrawn and filtered on a Whatman filter membrane (pore size: 1.2  $\mu\text{m}$ ), and the filtrates were analyzed for vanadium content. The vanadium concentration was determined using an inductively coupled plasma atomic emission spectrometer ICP-AES Jobin Yvon JY 2000 (Jobin Yvon, France).

Sorption isotherms were obtained by mixing known amounts of chitosan with fixed volumes of solutions containing varying concentrations of vanadate. The pH was regularly monitored and controlled with micro-volumes of either sulfuric acid or NaOH solutions (4 M).

Sorption capacity, given as the concentration of vanadate in the sorbent (mg V g<sup>-1</sup>, or mmol V g<sup>-1</sup>) was obtained by the mass balance equation:  $q = (C_o - C_{eq})V/m$ , where  $V$  is the volume of the solution,  $m$  is the mass of sorbent,  $C_o$  and  $C_{eq}$  are the concentrations in the solution at time  $t = 0$  and at equilibrium, respectively. The distribution coefficient,  $D$  (L Kg<sup>-1</sup>), was calculated as the ratio of V(V) concentration in the solid to the residual concentration in the solution.

Sorption kinetics were performed in a jar-test system at 20 °C, by mixing 1 L of solution (initial concentration: either 50 or 200 mg V L<sup>-1</sup>) with 250 mg of chitosan. The pH was fixed at the selected pH (either pH 3 or pH 6) and controlled during the sorption process. Samples were

regularly withdrawn and analyzed for vanadium content using ICP-AES.

**Desorption Procedure.** Samples were loaded with vanadium at different pHs. The initial concentration for the sorption process was 200 mg V L<sup>-1</sup> and 100 mg V L<sup>-1</sup>. Loaded sorbents were filtered, rinsed, dried at 60 °C, and brought into contact with 200 mL of water solutions for 4 days at the same pH as had been used for the loading. The pH was controlled using H<sub>2</sub>SO<sub>4</sub> or NaOH. The samples were then filtered and the filtrate was analyzed for vanadium content. A mass balance was used to calculate the desorption efficiency and the distribution coefficient. In a complementary experiment, a known amount of chitosan was brought into contact with 5 L of a vanadate solution at pH 3 (initial metal concentrations: 200 and 100 mg V L<sup>-1</sup>) for 4 days. The pH of the solution was controlled with sulfuric acid. The solution was filtered at equilibrium, the filtrate was analyzed, and the sorbent was rinsed with demineralized water and finally dried at 60 °C overnight. The final weight was measured. The sorption capacity (determined by the mass balance equation) was between 300 and 320 mg V g<sup>-1</sup>. The metal concentrations in the solid (including both the metal and the sorbent) were approximately 181 and 230 mg V g<sup>-1</sup>, depending on the initial concentration selected for sorption process. 100 mg of loaded sorbent were brought into contact for 4 days with 200 mL of water at different pHs (controlled with sulfuric acid): the same pHs as for the sorption procedure were selected. Finally, the solution was filtered and the filtrate was analyzed for V content. The efficiency of desorption was calculated using the mass balance equation. The objective of this study was to observe the distribution of vanadate during the desorption procedure, and to determine whether the sorption is reversible or not. Complementary desorption experiments were performed at pH 10 to pH 14 using sodium hydroxide solutions (0.1, 1, 10, 100, and 1000 mM).

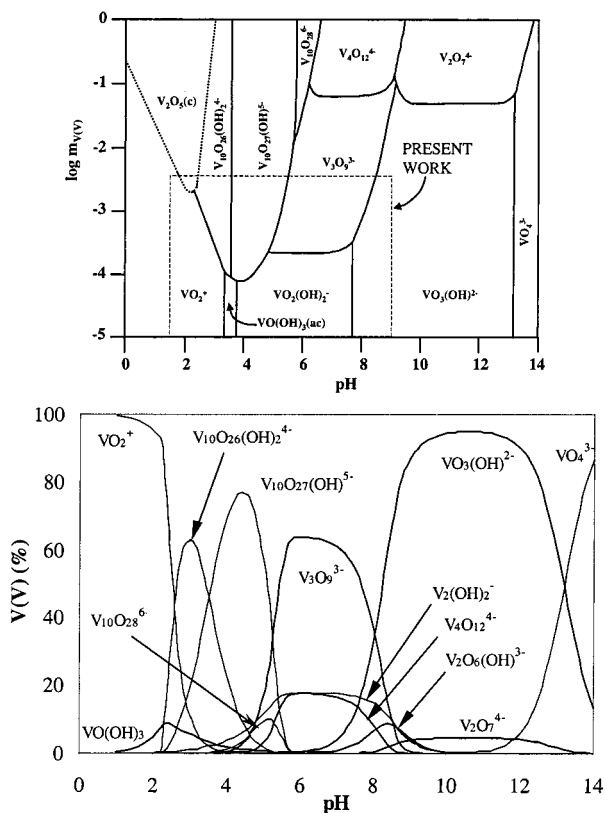
### Results and Discussion

**Vanadate Speciation.** Baes and Mesmer<sup>21</sup> have plotted the predominance diagram for vanadium (V) species. This diagram was used to select experimental pHs when vanadate concentration was varied between 0 and 200 mg L<sup>-1</sup>. Experiments were performed at pH 1.5, pH 3, pH 4.5, pH 5.2, pH 6, pH 7.5, and pH 9. Under these experimental conditions, vanadium ions do not precipitate. Figure 1 shows this predominance diagram and the ranges of pH and metal concentrations that were investigated in this study. Vanadium (V) can form 12 different soluble species under standard experimental conditions. The hydrolysis constants for these species given by Baes and Mesmer<sup>21</sup> were used to plot the species distribution diagram for vanadium (V), as a function of pH at different total vanadium concentrations. Figure 1 shows the diagram for a total vanadate concentration of 1 mM. It is noteworthy that the speciation of vanadium(V) is very complex: at each pH, several species may coexist, though whatever the pH more than 90% of total vanadium consists of 2 or 3 species (Figure 2).

**Influence of pH on Sorption Capacity and Distribution Coefficient.** Figure 3 shows the variation of sorption capacity with pH for standard experimental conditions. The sorption capacity remains almost null up to pH 2, then the sorption strongly increases up to pH 3. Above pH 3, sorption capacity decreases again and a break in the slope of the curve is observed at pH 6.5. Inoue et

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**Figure 1.** Predominance diagram for vanadium (V) (top) and distribution of vanadium (V) species as a function of pH (Ionic strength: 1 M; total vanadium concentration: 1 mM, calculated from constants given by Baes and Mesmer [21]) (bottom).

al.<sup>22</sup> compared the influence of pH on molybdate sorption by chitosan with the influence of pH on solvent extraction of molybdate and concluded that it is related to the presence of poly-oxoanions. Similar trends were observed for the plot of the decimal logarithm of the V(V) distribution coefficient versus the pH (not shown). It showed that at pH 1, the distribution coefficient is significantly lower than for other pHs (below  $10^3$  L Kg<sup>-1</sup>): at this pH, vanadate is only present in the form of VO<sub>2</sub><sup>+</sup>, which cannot be exchanged on protonated amine groups. By increasing the pH, the proportion of the decavanadate form of vanadium increases (Figures 1–2) and the sorption is more efficient: the distribution coefficient reached  $10^{4.5}$  L Kg<sup>-1</sup> at the optimum pH (pH 3 – pH 3.5). A similar influence of pH on sorption with regard to metal speciation has been cited in several studies, in relation with the formation or disappearance of adsorbable metal species.<sup>23–25</sup>

Experimental results may be partly explained by the protonation properties of chitosan, since vanadium sorption is thought to occur through ion exchange mechanisms: under the experimental conditions selected for this study (except pH 1.5), the V(V) in the solution is mainly in the form of anionic vanadate species. In acidic solutions, amine groups of chitosan are protonated (R–NH<sub>3</sub><sup>+</sup>) and vanadate anions can be exchanged with counterions bound to protonated sites. Sorlier et al.<sup>26</sup> recently showed that

the pK<sub>a</sub> of chitosan depends on the deacetylation degree of chitosan and to the degree of neutralization of the biopolymer ( $6.44 < pK_a < 7.1$ ). With a deacetylation degree of 87%, the pK<sub>a</sub> of chitosan tends to 6.5. Consequently, below pH 4.5, all accessible amine groups are protonated (Figure 3). At pH 5.2, about 95% of amine groups are protonated, while at pH 6, protonation level decreases to 76%. At pH 7.5, only 9% of amine groups are protonated, while at pH 9, all the amine groups are deprotonated. At pH 9, anion exchange cannot take place and vanadate anionic species are not adsorbed. At pH 7.5, sorption capacity tends to 45–60 mg V g<sup>-1</sup>, this is about 8–10 times lower than the level reached at the optimum pH. This fraction is similar to the actual fraction of protonated amine groups. At pH 6, sorption capacity tends to 310 mg V g<sup>-1</sup>, which is about 73% of the maximum sorption capacity reached at pH 3, and comparable to the protonation ratio of chitosan at this pH, ca. 76%. At pH 5.2, sorption capacity tends to 330 mg V g<sup>-1</sup>, which is 78% of the maximum sorption capacity at pH 3, while protonation is about 95%. At pH 4.5, sorption capacity tends to 390 mg V g<sup>-1</sup>. This is about 10% lower than the level reached at pH 3, though all amine groups are protonated.

**Sorption Isotherms.** Figure 4 shows the sorption isotherms obtained at selected pHs. Sorption isotherms at pH 1.5 and pH 9 are not shown to avoid overloading the figure: at these pHs, sorption capacity was lower than 20 mg V g<sup>-1</sup>. Chitosan is very efficient at removing vanadate: sorption capacity reached 400–450 mg V g<sup>-1</sup> (8–9 mmol V g<sup>-1</sup>). This value is comparable to results obtained with glutaraldehyde cross-linked chitosan beads.<sup>14</sup> It is noteworthy that the sorption affinity is very high, as shown by the initial slopes of the curves. The isotherms are characterized by a steep initial curve followed by the appearance of a plateau: the shape of the curve is similar to the Langmuir-type curve. At all pHs between pH 3 and pH 5.2, the maximum sorption capacities are comparable, but the affinity coefficient (initial slope of the curve) decreases with increasing pH. At pH 3, the shape of the isotherm curve is very favorable (almost irreversible), the favorability of the isotherm decreases with increasing pH. At pH 6, sorption is very low, almost negligible, up to a residual concentration for which the sorption progressively increases. The sorption isotherms begin with an unfavorable section, which is followed by a favorable section. At pH 7.5, sorption capacity was only 45–60 mg V g<sup>-1</sup>, irrespective of residual vanadate concentration.

Similar shapes of the sorption isotherms have been observed in the sorption of molybdate on chitosan, and the sorption was correlated to the presence of polynuclear hydrolyzed species. Twelve vanadium species can coexist in solution, however it is possible to categorize these species in several classes, such as cationic species (VO<sub>2</sub><sup>+</sup>), neutral species (VO(OH)<sub>3</sub>), anionic species with 2 subclasses: decavanadate species (V<sub>10</sub>O<sub>26</sub>(OH)<sub>2</sub><sup>4-</sup>, V<sub>10</sub>O<sub>27</sub>(OH)<sub>5</sub><sup>-</sup>, V<sub>10</sub>O<sub>28</sub><sup>6-</sup>) and other mono- or polyvanadate species (VO<sub>2</sub>(OH)<sub>2</sub><sup>-</sup>, VO<sub>3</sub>(OH)<sub>2</sub><sup>-</sup>, VO<sub>4</sub><sup>3-</sup>, and V<sub>2</sub>O<sub>6</sub>(OH)<sup>3-</sup>, V<sub>2</sub>O<sub>7</sub><sup>4-</sup>, V<sub>3</sub>O<sub>9</sub><sup>3-</sup>, V<sub>4</sub>O<sub>12</sub><sup>4-</sup>, respectively). The speciation of vanadium may influence (a) the relative ionic charge of metal anions (RIC: ionic charge divided by the number of vanadium units in the complex (*n*)), (b) the adsorbability of vanadate species on the chitosan biopolymer. The sorption isotherms were drawn versus (a) the total vanadium concentration in solution, (b) the concentration of decavanadates, and

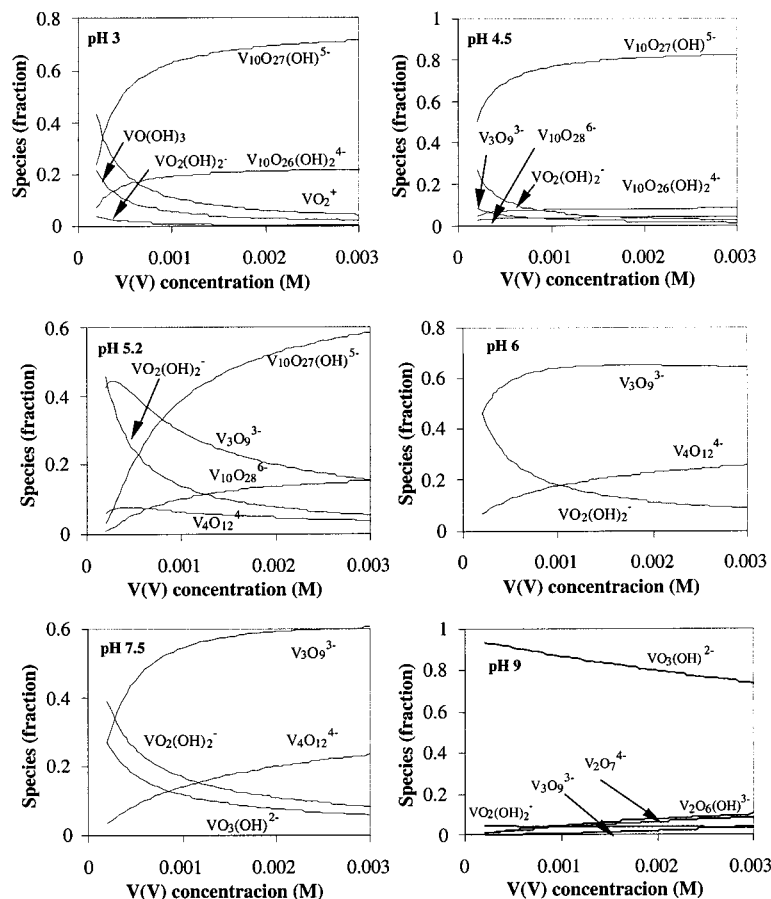
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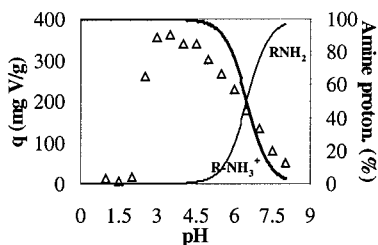
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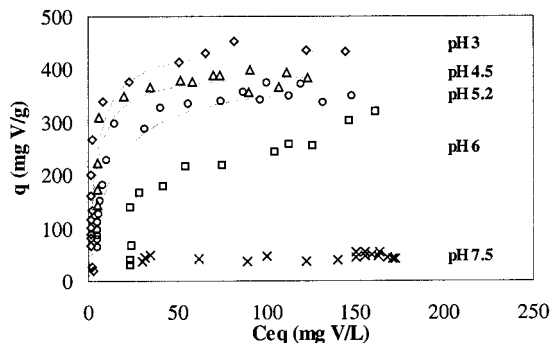
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**Figure 2.** Distribution of main vanadium (V) species at selected experimental pHs.



**Figure 3.** Influence of pH on vanadium (V) sorption capacity and amine protonation.



**Figure 4.** Influence of pH on vanadium (V) sorption isotherms (lines represent the modeling of experimental data (points) using the Langmuir equations and the parameters from Table 1).

(c) the concentration of total polynuclear anionic species (including decavanadate species). For this purpose, the data from sorption isotherms were plotted using the sorption capacity in function of the corrected concentration. For each residual concentration, the actual concentration

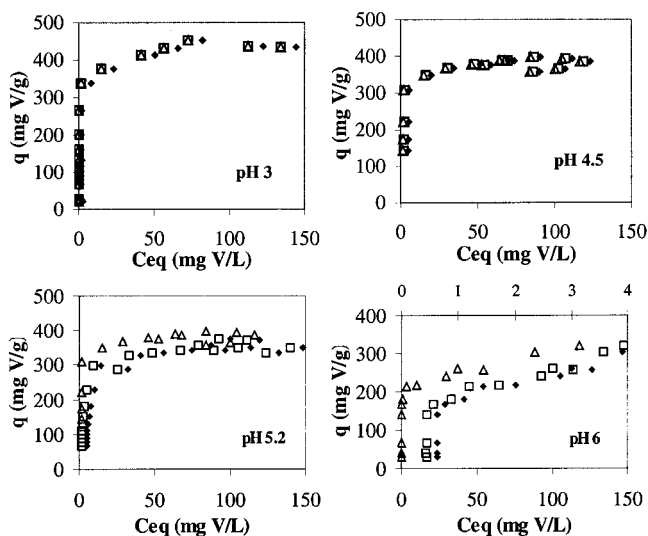
**Table 1. Sorption Isotherms – Langmuir Parameters**

pH	$q_m$	$b$	$R^2$
3	449.5	0.228	0.998
4.5	398.3	0.238	0.995
5.2	390.9	0.080	0.988

<sup>a</sup>  $q_m$ : mg g<sup>-1</sup>,  $b$ : L mg<sup>-1</sup>.

in either decavanadate or polynuclear anionic species was used instead of the total concentration (Figure 5), these curves were superimposed on the conventional isotherm curve ( $q = f(C_{eq, total})$ ).

At pH 3, all the curves are superimposed and characterized by the Langmuir-type shape (steep increase in sorption capacity and a plateau). The superimposition of the curves is explained by the predominance of decavanadate species at this pH whatever the total vanadate concentration. At pH 4.5 and low residual concentration, the curve is characterized by a shift: the sorption capacity tends to 0 for a nonnull residual concentration. This trend does not appear when the sorption capacity is plotted versus the concentration of either decavanadate or polynuclear species (the most part of polynuclear species is in the form of decavanadate). It is much more apparent at pH 5.2 for which the shift is increased, moreover, unlike other acidic pH, the curves plotting the sorption capacity versus decavanadate concentration and polynuclear species do not overlap perfectly. At pH 6, the sorption isotherm has a typical sigmoid shape, as was previously observed on molybdate sorption on chitosan.<sup>16</sup> At low residual concentration, sorption is almost null and the sorption isotherm is unfavorable; increasing the residual concentration results in a steep increase in sorption capacity (less steep than for acidic solutions). This change in the



**Figure 5.** Sorption isotherms and vanadate speciation: sorption isotherms plotted in function of total metal concentration ( $\blacklozenge$ ), decavanadate concentration, ( $\triangle$ ) and polynuclear species ( $\square$ ) (at pH 6, vanadate concentration appears on the top  $x$ -axis for the isotherm curve plotted versus decavanadate concentration).

shape of the molybdate sorption isotherm was correlated to the appearance of polynuclear species, which have been identified as the only adsorbable species. In the case of vanadate, several different forms of polynuclear species may coexist: decavanadate species and other polyvanadate species (where the number of vanadium units  $n \leq 4$ ). Comparison of the isotherm curves for different plots indicates that, at pH 6, the sorption isotherm curve only has a very steep initial slope (without the unfavorable section) when the sorption capacity is plotted versus decavanadate concentration. Chitosan has a greater affinity for decavanadate species than for other polynuclear species.

**Interpretation of Sorption Mechanism – Influence of Ionic Balance.** Juang and Ju,<sup>28</sup> and Lasko and Hurst<sup>19</sup> observed that the chelation of metal ions with ligands changes the electrostatic interactions of chitosan with these ions. A similar effect concerning vanadium speciation may explain the influence of pH on sorption isotherms. Metal anion exchange may be controlled by the relative ionic charge (RIC) of the species. The RIC is higher for the polynuclear species with a lower number of vanadium units ( $n \leq 4$ ) than for decavanadate species. For decavanadate species, the RIC varies between  $-0.4$  and  $-0.6$ , depending on the hydroxylation level, while for other polynuclear anionic species, the RIC ranges between  $-1$  and  $-2$  (the RIC varies between  $-2$  and  $-3$  for mononuclear vanadate species). On the other hand, the maximum sorption capacity reached  $8\text{--}9 \text{ mmol V g}^{-1}$ , taking into account the deacetylation percentage of chitosan; the molecular weight of the equivalent-monomer unit is ca.  $166 \text{ g}$ , so the molar ratio between V and  $-\text{NH}_2$  groups is  $1.3\text{--}1$ . This ratio does not take into account actual accessibility to amine groups, which can be decreased by the residual crystallinity of the sample.<sup>27</sup> When the sorbent is saturated, the excess of vanadium relative to amine groups confirms that vanadium is adsorbed in a polynuclear form. With polynuclear vana-

date species of low vanadate unit number ( $n \leq 4$ ), vanadate anions are closely adsorbed to each other and the high charge density may result in repulsion phenomena; in this sense the sorption of decavanadate decreases steric and ionic hindrance by increasing the space between occupied amine groups. The repulsion between adsorbed vanadate ions is thus reduced. For the same exchange capacity (related to the ionic charge of the sorbent), the number of exchanged or attracted vanadium species increases with decreasing RIC. On the other hand, other interactions may occur, those that stabilize metal-sorbent links: hydroxyl linkages have been suggested for molybdate interaction with chitosan. The reaction of molybdate species with different units of the polymer has been suggested for the coagulation of chitosan solutions within molybdate solutions: the reaction of several units of the biopolymer with the same heptamolybdate unit is suspected to cause the cross-linking of the biopolymer.<sup>29</sup> Similar interactions may occur with vanadate.

**Sorption Kinetics.** Metal speciation may also control sorption kinetics through diffusion limitations. The formation of polynuclear species increases the ionic size of metal ions, which, in turn, reduces diffusivity in the solid.<sup>30</sup> Figure 6 shows several curves presenting sorption kinetics under selected experimental conditions. To see whether metal speciation influences the sorption rate, two different pHs are tested (pH 3 and pH 6) at low initial concentrations (LC:  $50 \text{ mg V L}^{-1}$ ) and high initial concentration (HC:  $200 \text{ mg V L}^{-1}$ ). Top (complete kinetics) and middle (initial sorption step) curves show the change in the relative concentration in the solution in function of contact time. The bottom curve presents the fractional approach to equilibrium (FATE) for the initial step of the sorption process in function of the square root of time. FATE is the ratio of the concentration in the solid at time  $t$  divided by the concentration in the solid at equilibrium. Using the FATE reduces the influence of the difference in the saturation of the sorbent on the kinetics. It is noteworthy that sorption kinetics are faster at pH 3 than at pH 6 and that the time required to reach equilibrium increases with metal concentration. While ca.  $10 \text{ h}$  are sufficient to achieve complete sorption at pH 3 with an initial concentration of  $50 \text{ mg V L}^{-1}$ , 3 days of contact are necessary to reach equilibrium at pH 6 with a metal concentration of  $200 \text{ mg V L}^{-1}$ . The plot of the FATE versus the square root of time shows that for low concentration solution at pH 3 the slope of the curve is significantly higher than that obtained at pH 6 or at pH 3 with high concentration of vanadium. Morris and Weber<sup>31</sup> used the plot of  $q(t)$  versus the square root of time to measure an overall intraparticle diffusion rate. Plotting the FATE versus the square root of time gives a similar measure of the relative intraparticle diffusion rate ( $k, \text{min}^{-1/2}$ ):

$$\frac{q(t)}{q_{\text{eq}}} = k t^{1/2} + k'$$

The parameter  $k'$  is a constant related to the thickness of the external layer surrounding the particle in which the external diffusion resistance takes place. The pseudo

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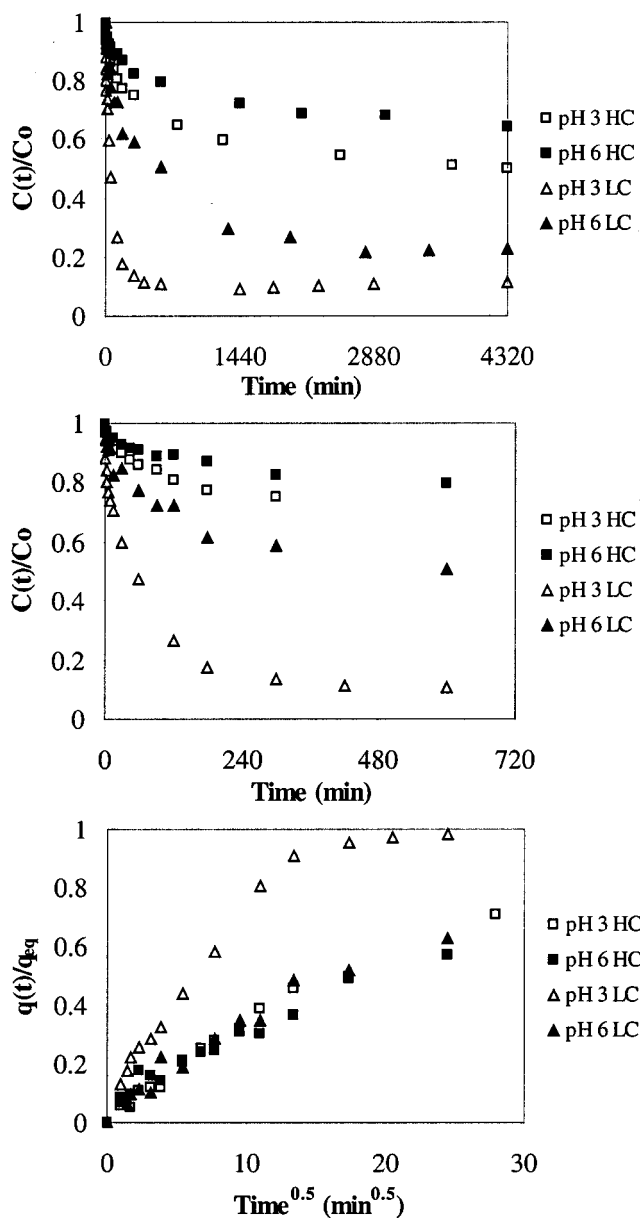
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**Table 2. Kinetic Parameters – Influence of pH and Metal Concentration**

pH	[V] (mg V L <sup>-1</sup> )	10 <sup>2</sup> <i>k</i> (min <sup>-1/2</sup> )	10 <sup>2</sup> <i>K</i>	<i>R</i> <sup>2</sup>	10 <sup>3</sup> $\alpha$ (min <sup>-1</sup> )	10 <sup>2</sup> $\alpha_0$	<i>R</i> <sup>2</sup>
3	50	5.42	12.57	0.969	8.87	19.90	0.993
3	200	3.04	2.52	0.978	2.11	3.36	0.960
6	50	2.36	7.91	0.969	2.26	8.54	0.939
6	200	1.76	10.70	0.976	0.52	5.08	0.912

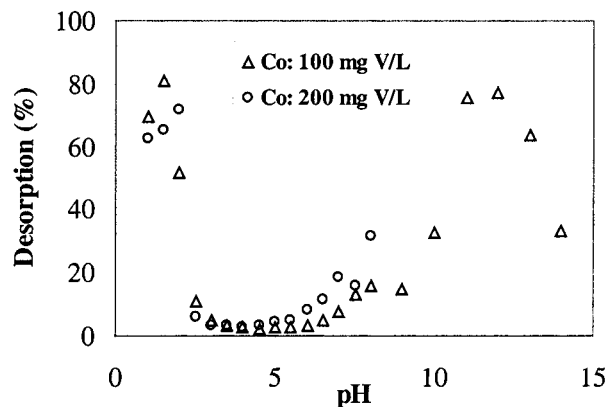


**Figure 6.** Vanadium(V) sorption kinetics – Influence of pH (3 and 6) and metal concentration (HC: 200 mg V L<sup>-1</sup> and LC: 50 mg V L<sup>-1</sup>).

first-order kinetic equation was also used by Findon et al.<sup>32</sup> for the evaluation of the initial sorption rate ( $\alpha$ , min<sup>-1</sup>),  $\beta_L$  is the external diffusion coefficient, and *S* is the superficial area of the sorbent:

$$\ln \frac{C(t)}{C_0} = \alpha t + \alpha_0 \approx \beta_L S t$$

The parameter  $\alpha_0$  is similar to the parameter *K* and it is a function of the thickness of the external layer. These



**Figure 7.** Influence of pH on the desorption of vanadium from V(V)-loaded chitosan – experiments performed with sorbent loaded with different initial concentrations (*C*<sub>0</sub>: 100 or 200 mg V L<sup>-1</sup>).

simple equations are sufficient to give a first approximation of kinetic rates and to allow the sorption rates to be compared for different experimental conditions. Table 2 lists the coefficients and correlation coefficients for the kinetic experiments, using the FATE and the pseudo first-order equation. As shown in Figures 1 and 2, at pH 6 the main form of vanadium in the solution is V<sub>3</sub>O<sub>9</sub><sup>3-</sup>, especially at high metal concentration. At low concentration, such as at the end of the sorption step, the VO<sub>2</sub>(OH)<sub>2</sub><sup>-</sup> species may coexist in significant concentration. At pH 3 and high metal concentration, V<sub>10</sub>O<sub>26</sub>(OH)<sub>2</sub><sup>4-</sup> is the predominant vanadium species, while reducing metal concentration leads to the appearance of cationic species, VO<sub>2</sub><sup>+</sup>, which are not adsorbable. The sorbent has a great affinity for vanadate in acidic solutions: at low concentration, there is a large excess of sorption sites at the sorbent surface and the sorption rate is very fast. The increase in the contact time results in a decrease in the residual metal concentration and the formation of less adsorbable species. Increasing metal concentration decreases the excess of sorption sites: the sorption sites are saturated faster than at low concentration. Consequently, after a long contact time, the gradient between the surface of the solid and the solution progressively decreases and becomes less favorable to the transfer of metal ions to the sorbent. In this case, the speciation is not a very important parameter since the predominant vanadate species do not vary throughout sorption process. At pH 6, vanadate takes the form of less adsorbable species (tri- or mono-vanadate species). As polymer protonation decreases, the sorbent has a lower affinity for the predominant vanadate species than for those that predominate at pH 3 and the sorption kinetics is slowed.

**Desorption.** Figure 7 shows the influence of pH on vanadium desorption from the loaded sorbent. Since metal speciation is favorable at pH 3.0 to pH 3.5 we would expect the metal ion-sorbent interaction to be stable in this pH range. On the other hand, above and below this pH range the affinity of the sorbent for metal ions is weaker and the vanadium release can be expected to increase. Experimental data show that above pH 3.5, vanadate desorption progressively increases. However, the sorption is not

(32) Findon, A.; McKay, G.; Blair, H. S. *J. Environ. Sci. Health* **1993**, *A28*, 173–185.

completely reversible at any pH. Even under the most favorable desorption conditions, efficiency does not exceed 80%. At pH 2.5–5.5, desorption does not exceed 7–8%. Figure 1 shows that in this pH range, vanadium predominately takes the form of decavanadate species, which have a great affinity for the sorbent. Consequently, vanadium is stable on the sorbent. In this pH range, the concentration of counterions (brought by the acid used for pH control) is below 1 mM, and the competition effect is not strong. When the pH increases above pH 5.5, less adsorbable species predominate in the solution. This displaces the metal ion from the solid to the solution: the desorption efficiency increases. Moreover, above this pH the ionic exchange capacity decreases because of the deprotonation of amine groups. For pHs below pH 2.5, the sharp increase in desorption efficiency may be related to both the speciation of vanadium in solution and to the strong competitor effect of counterions caused by the acid used to control pH. The distribution coefficients were calculated for each pH using a mass balance equation (not presented). They are systematically higher than those obtained during the sorption process (at similar pH). This result confirms that the sorption process is not perfectly reversible. Increasing the pH from 8 to 12 also increases the desorption efficiency, however even at the optimum pH (pH 12), complete desorption is not achieved. In alkaline solutions, the amine groups are completely deprotonated and the sorbent is unable to interact with anionic species:  $\text{VO}_3(\text{OH})^{2-}$  predominates in solution. Surprisingly, above pH 12, vanadium desorption decreases again.

### Conclusions

Chitosan is very efficient at removing vanadate anions from dilute solutions through electrostatic attraction and anion exchange in acidic solutions. The optimum pH was found to be in the range pH 3.0 to pH 3.5. Sorption capacity under optimum experimental conditions reaches 8–9 mmol V  $\text{g}^{-1}$  (ca. 400–450 mg V  $\text{g}^{-1}$ ), which corresponds to a molar ratio of ca. 1.3–1.5 between V and  $-\text{NH}_3^+$  groups. This stoichiometric ratio, together with the shape of the sorption isotherm curves, which was correlated to

the predominance of anionic species, indicates that sorption occurs through the reaction of protonated amine sites with decavanadate species (preferentially to other polynuclear anionic species of lower vanadium unit number). In acidic solutions, the predominance of decavanadate solutions leads to almost rectangular sorption isotherm curves. In near neutral solutions, the predominance of nonadsorbable vanadate species results in negligible adsorption up to a concentration, dependent on pH, at which decavanadate species appear in solution. At this limit residual concentration, sorption capacity steeply increases. Above pH 7, the protonation of amine groups is significantly reduced and the polymer is not able to exchange counteranions with vanadate species or to attract anionic species. Thus, the protonation of the polymer reveals a key parameter, as does the distribution of metal species, on the efficiency of vanadium sorption on chitosan. Decreasing the  $\text{p}K_a$  of chitosan by a chemical modification or using other polymers with lower  $\text{p}K_a$  would enhance sorption performance, with respect to metal distribution and the presence of adsorbable metal species: the presence of highly charged polynuclear species with large ionic size is suspected to induce multiple linkages with different units of the polymer chain.

Sorption kinetics is also strongly controlled by the pH and the metal concentration. The predominance of decavanadate species has been correlated to the fastest kinetics.

Desorption is optimum in alkaline solutions, in which vanadium takes the form of vanadate species in solution. Increasing the pH results in deprotonation of the biopolymer, which is not ready for anion sorption. In acidic solutions, vanadate release is not complete: the distribution coefficient is greater than the distribution coefficient obtained during this sorption step.

**Acknowledgment.** J.G. thanks CONACYT and CONCYTEG (N° 99-16-203-201 An.2) for fellowship. Authors thank the Franco-Mexican Program PCP (N° 99/4) for financial support.

LA010802N