

LC-ICPMS speciation and adsorption of vanadium ions by Ca-Fe(III) alginate beads

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Resumen

Los iones de V(IV) y V(V) son especies tóxicas para el medio ambiente y la salud humana. En este estudio evaluamos el uso de perlas de alginato de Ca-Fe(III) como adsorbentes para la eliminación de dichos iones de soluciones acuosas. La inserción de hierro en la matriz de Ca-alginato como hidróxido férrico coloidal disperso aumentó la eficiencia de adsorción correspondiente hacia esos iones al mejorar la adsorción. El comportamiento de adsorción se ajustó mejor al modelo de isotermas de Freundlich. El parámetro k de Freundlich, que indica la capacidad de absorción relativa del adsorbente para V(IV) y V(V) fueron $0.198 \text{ (mg/g)(L/mg)}^n$ y $0.899 \text{ (mg/g)(L/mg)}^n$ respectivamente. Nuestros resultados sugieren que el principal mecanismo de eliminación de iones de vanadio se debió a la formación de complejos de esfera externa. Nuestros resultados demuestran que las perlas de alginato de Ca-Fe (III) representan un adsorbente eco amigable, que se puede utilizar para remediar los niveles traza de iones de V(IV) y V(V) de agua residual y potable contaminadas.

Palabras clave: vanadio, perlas de alginato de Ca-Fe(III), adsorción, LP-ICP-MS, especiación

Abstract

V(IV) and V(V) ions are toxic species to the environment and human health. In this study we evaluated the use of Ca-Fe(III) alginate beads as adsorbents for the removal of such ions from aqueous solutions. The insertion of iron into the Ca-alginate matrix as a dispersed colloidal ferric hydroxide increased the corresponding adsorption efficiency towards those ions by enhancing adsorption. The adsorption behavior was best fitted by the Freundlich isotherms model. The Freundlich parameter k , which indicates the relative uptake capacity of the adsorbent for V(IV) and V(V) were $0.198 \text{ (mg/g)(L/mg)}^n$ and $0.899 \text{ (mg/g)(L/mg)}^n$ respectively. Our results suggest that the main mechanism of removal of vanadium ions was due to the formation of outersphere complexes. Our results demonstrates that Ca-Fe(III) alginate beads represents a green adsorbent, which can be used to remediate trace levels of V(IV) and V(V) ions from contaminated drinking and wastewaters.

Keywords: vanadium, Ca-Fe(III) alginate beads, adsorption, LP- ICP-MS, speciation

1. Introduction

Vanadium toxicity to humans and wildlife are dependent on their bioavailability and chemical species (Cornelis *et al.* 2008; Baig *et al.* 2010). It has six different oxidation states (-I, 0, II, III, IV, and V). Their most stable forms in natural waters are V(V) under oxidizing conditions, and V(IV) under reducing environments. The V(IV) is stable as VO^{2+} or $\text{VO}(\text{OH})^+$ cation and V(V) as HVO_4^{2-} and H_2VO_4^- oxyanions. V(V) is more toxic than V(IV), and the V(IV) is not thermodynamically stable at pH greater than 7 (Pourret *et al.*, 2012; Giacomino *et al.* 2010; Zhang *et al.* 2008; Anirudhan *et al.* 2010; Peacock *et al.* 2004 and Pan *et al.* 2010). The occurrence of ions in the environment is mainly from anthropogenic sources such as: metallurgical processes, mining, fertilizers, pesticides, textiles, ceramics production, and petroleum related industries (Budinova *et al.* 2006; Ladeira *et al.* 2004; Kaczala *et al.* 2009; Yeom *et al.* 2009 and Loukidou *et al.* 2003).

Adsorption seems to be an inexpensive, easily to scale up, and with high removal efficiencies green alternative (Lenoble *et al.* 2002 and Guan *et al.* 2009). A variety of commercial and low-cost adsorbents such as: activated carbon and agricultural wastes have been studied for the removal of vanadium and others oxyanions (Gabler *et al.* 2009; Bhatnagar *et al.* 2008; Kaczala *et al.* 2009 and Shahri *et al.* 2010).

Ca-alginate beads had also been proven as efficient adsorbents for divalent cations such as Cu, Zn, Cd, Ni, Co (Pandey *et al.* 2002; Ibañez *et al.* 2002; and Kong *et al.* 2010) and also for organic contaminants such as triclosan (López-Morales *et al.* 2013). The addition of barium or iron dispersed into the Ca-alginate matrix enhances the removal efficiency toward anionic species such as vanadium ions. The alginate polysaccharide matrix has been chosen because it has the capacity to form hydrogels in presence of divalent cations (Barnejee *et al.* 2007). Although Banerjee *et al.*, Zouboulis *et*

al., Lim *et al.* and Min *et al.* have reported modified alginate beads as adsorbents for arsenic oxyanions, none reported adsorption isotherms, which are essential models to allow a feasible comparison with other reported adsorbents. Also, to our best knowledge, the adsorption isotherms of toxic ions such as vanadium using Ca-Fe(III) alginate beads have not been reported in the literature.

This research addresses these issues and included the Langmuir and Freundlich isotherms for V(IV), and V(V) ions using Ca-Fe(III) alginate beads as an environmentally friendly adsorbent. This study is also novel in reporting the point of zero charge (pH_{pzc}) for the Ca-Fe(III) alginate beads, which is an important parameter to understand the adsorption mechanisms via electrostatic attraction. Also, incorporates the competitive adsorption to confirm the columbic attraction between the adsorbent-ions interface. This study addressee in a novel approach the use of speciation with state-of-the-art instrumentation IP-ICPMS to verify the adsorption processes.

2. Materials and methods

2.1 Reagents

V(IV) solutions were prepared from vanadyl sulfate (ACROS Organics, 17-23% V); the V(V) solutions from ammonium metavanadate (ACROS Organics, 99.5%). Nitric acid (Fisher Co., Optima grade) and sodium hydroxide (Fisher Co., ACS grade) were used to regulate the pH. Ca-Fe(III)alginate beads were prepared using alginic acid sodium salt (MP Biomedicals LLC, low viscosity), calcium chloride dihydrate (Fisher Co., certified ACS grade), and ferric chloride hexahydrate (Ricca Chemical Co., ACS reagent grade). The solutions for competitive ions tests were prepared from sodium carbonate monohydrate (Alfa Aesar Co., ACS Grade, 99.5%), sodium phosphate monobasic (Fisher Co., Certified ACS Grade), and sodium sulfate (Fisher Co., 99.5% purity). The acids used for desorption tests were hydrochloric acid (Fisher Co., trace

metal grade) and sulfuric acid (Midland Scientific Inc., Baker grade). All solutions were prepared with distilled-deionized water at 18.2 MΩ.

2.2 Ca-Fe(III) alginate beads synthesis

The Ca-Fe(III) alginate beads were synthesized using the procedure described in Sánchez-Rivera *et al.* 2013, using a 2% w/v alginic acid solution by dropwise addition in 0.1M CaCl₂ and 0.02 M of FeCl₃ at slow (60 rpm) magnetic agitation. The pH was adjusted to 8.0 ± 0.1 and after 24 hours of contact time, the resulting beads were recovered by washing, vacuum filtrated and let to dry for three days at room temperature and humidity conditions.

2.3 Ca-Fe(III) beads characterization

Elemental analysis and size distribution

The iron and calcium concentrations in the Ca-Fe(III) alginate beads were determined by mass balance after elemental analyses of the aqueous solutions before and after the beads synthesis.

Also, the Ca-Fe(III) alginate beads were observed through an optical microscope (Nikon SMZ1500) to determine the average diameter as reported by Sánchez-Rivera *et al.* 2013.

Point of zero charge

In order to predict the net charge on the Ca-Fe(III) alginate beads surface at the studied pH, the point of zero charge (pH_{pzc}) was determined using the method described by Kumar *et al.*, 2008. Duplicate samples of 50 mL of NaCl 0.1M and 0.01M solutions were pH adjusted from 2-10 and subjected to 0.5g of the Ca-Fe(III) alginate beads and agitated in a shaker water bath at 200 rpm for a period of 48 hours. Finally, the pH was recorded and a graph of (pH_o - pH) vs. pH_o was constructed, where the intersection with the abscissa axis is called the pH_{pzc} (Kumar *et al.* 2008).

EDAX Analysis

The Ca-Fe(III) alginate beads and Ca-Fe(III) alginate beads loaded with vanadium ions were analyzed without further sample preparation by Energy disperse X-ray fluorescence spectroscopy (EDAX) with a SEM (JEOL 6480LV).

2.4 Adsorption tests

Duplicates solutions of V(IV), and V(V) (100-2000 ppb) were independently contacted with 5g/L of Ca-Fe(III) alginate beads at various pH (2, 4, 6, 8, and 10) until equilibrium was reached, generally 24 hours. All solutions were placed in plastic 125 mL sealed bottles at room temperature (298K) in a water shaker bath and agitated at 200 rpm for a period up to 24 hours. Aliquots of 1.00 mL were withdrawn at different time intervals until 24 hours equilibrium time. All samples were quantitatively analyzed in triplicate using an Agilent ICP-MS 7500 ce system using scandium as an internal standard. Method blanks and matrix spikes were run in each batch of ten samples allowing a 15% relative error for quality control purposes. All experiments were performed in duplicate.

2.4.1 Competitive studies

Duplicate solutions of V(IV) and V(V) at 100 ppb were independently contacted with sulfate, carbonate and phosphate ions at diverse ratios of competitive ions (Oxyanion: Competitive Oxyanion; 1:1, 1:3 and 1:5) with 5g/L of Ca-Fe(III) alginate beads at pH 6.0 ± 0.1. These solutions were processed as a regular adsorption experiment as detailed in section 2.4.

2.4.2 Adsorption isotherms

Freundlich isotherm is described by a power function, which relates at a constant temperature the amount of adsorbed species as a logarithmic function of the remaining concentration at equilibrium in the liquid phase. This isotherm applies toward a reversible equilibrium at short equilibration times (seconds

to minutes). This isotherm is based on a multilayer adsorption on an heterogeneous surfaces and assumes that the adsorption sites are distributed exponentially with respect to the heat of adsorption as described by Equation 1:

$$q_e = k C_e^{1/n} \quad (1)$$

The above equation can be expressed in a linear model as follows:

$$\ln q_e = \ln k + 1/n \ln C_e \quad (2)$$

where k ((mg/g)(L/mg)ⁿ) and n are Freundlich constants, which describe the relative adsorption capacity of the adsorbent and the intensity of adsorption, respectively. The n constant, which varies with the heterogeneity of the adsorbent, is also calculated from the experimental data. The greater the $1/n$ value indicates a better adsorption process between the adsorbent and the solute (Proctor *et al.* 1996 and Lim *et al.* 2007).

Langmuir isotherm model describes that all adsorption sites are energetically homogeneous and forms monolayer coverage within the adsorbent surface. It also establishes that the adsorption occurs with no lateral molecules interactions and when saturation occurs no further adsorption could be achieved. The Langmuir model is expressed using the Equation 3:

$$q_e = q_{max} b q_e / (1 + b C_e) \quad (3)$$

The above equation can be expressed in a linear model as follows:

$$C_e/q_e = (1/q_{max}) C_e + 1/q_{max} b \quad (4)$$

where the q_{max} and b are Langmuir constants, which represent the adsorption capacity of the adsorbent (mg/g) and the affinity of the solute for the adsorbent surface (L/mg), respectively. The C_e and q_e represent the concentration of the solute ions (mg/L), and the adsorption capacity of the sorbent (mg/g) at equilibrium, respectively (Zheng *et al.* 2009;

Allen *et al.* 2004 and Guo *et al.* 2009). The ions concentrations at equilibrium were graphed using the Langmuir and Freundlich isotherms models in order to determine the best model for the system.

2.4.3 LC ICPMS Speciation

Table 3 shows the general experimental conditions for the vanadium speciation. The speciation was carried out using a HPLC Agilent 1100 equipped with a quaternary pump using a C₁₈ column connected via PEEK capillary tubing to the peristaltic pump of the ICPMS Agilent 7500. The ICPMS was run in the time resolved analysis mode. The separation was achieved using a isocratic elution of a mobile phase compose of 2.5mM ethylenediaminetetraacetic acid (EDTA), 10 mM tetra butyl ammonium hydroxide (TBAOH), 60mM ammonium acetate (AC) and 10 mM ammonium phosphate dibasic ((NH₄)₂HPO₄) at pH 6.73. The TBAOH was used as an ion pair agent to use a reverse phase chromatography column.

2.4.4 Desorption studies

Ions species adsorbed onto the Ca-Fe(III) alginate beads were desorbed using 0.1M nitric, hydrochloric, and sulfuric acids in a rotamix at 30 rpm for a period of 24 hours. To calculate the desorption of the ions, aliquots were taken, diluted and analyzed by ICP-MS.

3. RESULTS AND DISCUSSIONS

3.1 Adsorbent characterization

Elemental analysis and size distribution

The elemental analysis of the Ca-Fe(III) alginate beads showed a content of 7.3 ± 0.3 % (w/w) of Ca and 0.5 ± 0.1 % (w/w) of Fe(III). The average diameter of the Ca-Fe(III)alginate beads was 2.2 ± 0.3 mm, which was reported by Sánchez-Rivera *et al.* 2013.

Point of zero charge

The pH_{pzc} for the Ca-Fe(III) alginate beads was 6.7 ± 0.3 as shown in Figure 1. Below this pH value (pH_{pzc}), the net charge on the beads surface tends to be positive, thus attracting the ions under study. The predominant ions species at pH below the pH_{pzc} are: V(V) the more stable form is $H_2VO_4^-$ (Sherry Li *et al.* 2007) and V(IV) is more stable in anoxic conditions and will oxidized slowly by air to V(V). Our results suggest that a columbic attraction is favorable at pH below the pH_{pzc} of 6.7, and this is the main mechanism of the adsorption of the studied ions.

EDAX Analysis

As seen on Figure 2a the main composition of the Ca-Fe(III) alginate beads are: C, O, Ca, Fe and Cl ions. When the vanadium ions are adsorbed on the Ca-Fe(III) alginate beads as shown in Figure 2b. the peaks of vanadium are observed in the EDAX spectra.

3.2 Competitive studies

As shown in Table 1, The removal efficiency for V(IV) and V(V) decreased from 100% sorption to 95-90% and 93-90% respectively for all levels of competitive ions. The concentration ratios (sorbent: competitive ion) tested were 1:1, 1:3 and 1:5 of phosphate, carbonate and sulfate as competitive ions. Statistical analysis for each concentration and ionic strength values at a 95% confidence level revealed a significant difference between the adsorption of the ions in presence/absence of competitive ions. These results suggest the adsorption behavior dependence when the ionic strength is increased up to $3.3-3.4 \times 10^{-5}$ (when phosphate is 3x) for competing ions species. This behavior infers the formation of an outer-sphere complex, which is formed quickly by electrostatic columbic attractions. Under this model other ions can compete with the non-specific available binding sites, therefore decreasing the removal efficiency as the ionic strength of competing ions increases. Also, the Chapman theory establishes that the adsorption process is affected by the presence of an

electrolyte by inducing an increase in the thickness of the electrical diffused double layer. Such enhancement inhibits the approaching of the adsorbate into the solute, thus decreasing its electrostatic attraction and removal efficiency (Zhang *et al.* 1990; Manohar *et al.* 2005 and Liu *et al.* 2008). However, it worth pointing out that even in the presence of other competing ions, the adsorption process remained above 90% for all species evaluated (V(IV) and V(V)). These results are very encouraging and suggest the potential application of the developed Ca-Fe(III) alginate beads for its efficient use in real contaminated effluents even in the presence of diverse competing ionic species.

3.3 Adsorption isotherms

The values for the Freundlich parameters n shown in Table 2 are between 1.01-1.56. The n values between 1 to 10 are indicative of a positive adsorption toward the adsorbent the Ca-Fe(III) alginate beads. Higher k values represent a better sorption capacity of the adsorbent toward the analyte (Patil *et al.* 2011). In this case, V(IV) and V(V) have k values of 0.198, and 0.899 respectively; V(V) showed the best adsorption capacity. Figure 2 shows the linear regression results for the Freundlich and Langmuir isotherms models. These results suggest that the more suitable model is the Freundlich by showing the best linear correlation coefficient. These results were as expected because the Freundlich model predicts a better adsorption on heterogeneous surface sites, which agrees with the non-specific binding mechanism such as electrostatic attraction and Van der Waals forces.

3.4 IP-ICPMS Speciation

The Figure 4a shows the IP-ICPMS chromatograms for the speciation of $150 \mu\text{g/L}$ of vanadium (V(IV), V(V)) inorganic species. After 2 hours of contact with 5g/L Ca-Fe(III) alginate beads at pH 6.0 (Fig. 4b) the V(IV) was removed 86% and V(V) was removed by 85% removal. Due to the fast and similar adsorption behavior, the adsorption results suggest a weak

solute-adsorbent interaction. Electrostatic interaction must be the major removal sorption between the negative V(V) species (HVO_4^{2-} and H_2VO_4^-) and the positive charge of Ca-Fe(III) alginate beads at pH 6.0. Instead, the adsorption of V(IV) species (VO^{2+} and $\text{VO}(\text{OH})^+$) is believed to be achieved by Van der Waals forces within the beads surfaces.

3.5 Desorption tests

The desorption of V(IV) and V(V) species varied from 90 to 100% using nitric, hydrochloric, or sulfuric acids. All species could be recovered from the Ca-Fe(III) alginate beads up to 91-100% using 0.1M of sulfuric acid as shows in Table 4. The Table 5 shows the liberation of calcium and iron from the alginate beads once had been processed with the acids. In the vanadium experiments, the results also showed that during the acids desorption experiments calcium ions are being released from the matrix in the range of 68.8-73.6% of their initial concentration. The results suggest that nitric and hydrochloric acids are the best acids to desorbed vanadium ions because less damage is caused to the Ca-Fe(III) alginate beads as evidenced by a lower release of calcium and iron ions. The desorption of vanadium ions from the Ca-Fe(III) alginate beads the use of less concentrated acids could reduced the dissolution of the calcium and iron from the alginate matrix.

4. CONCLUSIONS

The present study showed that Ca-Fe(III) alginate beads are effective in the removal of vanadium ions species at trace concentrations. The results suggest vanadium ions seems to be adsorbed onto the heterogeneous surface of the Ca-Fe(III) alginate beads as suggested from the Freundlich model. The results show when using competitive studies that the general mechanism of removal

was due by the formation of outer-sphere complexes such as columbic attraction within the V(V) species and by Van der Waals forces within the V(IV) species and the beads surface.

Both attraction modes are achieved by faster equilibrium and weak forces in comparison with other type of attraction such as inner sphere complexation. The pH_{pzc} demonstrated that below a pH of 6.7 ± 0.3 the net charge tends to be positive, thus reinforcing that columbic attraction is occurring at pH 6.0.

All the ions species could be recovered up to 91-100% when using 0.1M sulfuric acid. The liberation of calcium (up to 73.6%) and iron (up to 47.4%) from the Ca-Fe(III) alginate beads during the acid desorption suggests a matrix modification.

The results confirms the potential use of the Ca-Fe(III) alginate beads to remove trace amounts of vanadium ions in drinking and wastewaters in the presence of diverse competing ions (phosphate, carbonate and sulfate) which are present in natural water scenarios.

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Table 1. Removal efficiency of vanadium ions using 5g/L Ca-Fe(III)alginate beads in the presence with other ions

	V(IV)			V(V)			
	Ratio	% Removal	SD	t Student (95%)	% Removal	SD	t Student (95%)
CO₃²⁻	1:1	93	1	9.90	90	4	7.07
	1:3	93	1	9.90	90	2	7.07
	1:5	93	1	9.90	90	2	7.07
SO₄²⁻	1:1	93	1	9.90	91	1	12.71
	1:3	91	2	6.36	91	1	12.71
	1:5	90	1	14.14	91	1	12.71
PO₄³⁻	1:1	93	1	9.90	92	1	11.31
	1:3	94	1	8.48	93	1	9.90
	1:5	95	1	7.07	93	1	9.90

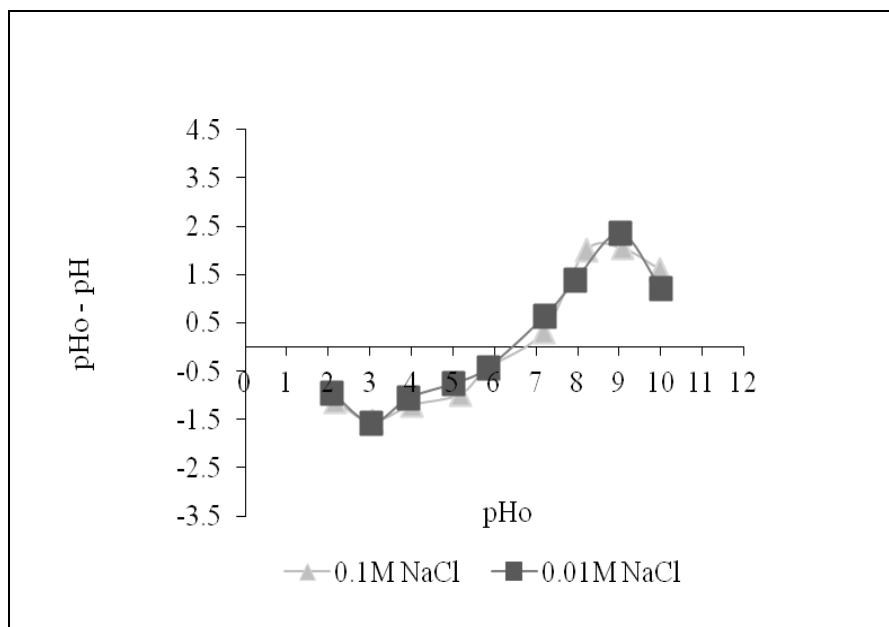


Figure 1. Point of zero charge graph for Ca-Fe(III) alginate beads in NaCl 0.1M and 0.01M

Table 2. Langmuir and Freundlich isotherms parameters for vanadium ions using 5g/L Ca-Fe(III)alginate beads

	<i>Langmuir</i>			<i>Freundlich</i>		
	q_{max} (mg/g)	B (L/mg)	R^2	k (mg/g)(L/mg) ⁿ	N	R^2
V(IV)	6.77	0.03	0.7466	0.198	1.01	0.9982
V(V)	0.799	2.93	0.9658	0.899	1.44	0.9840

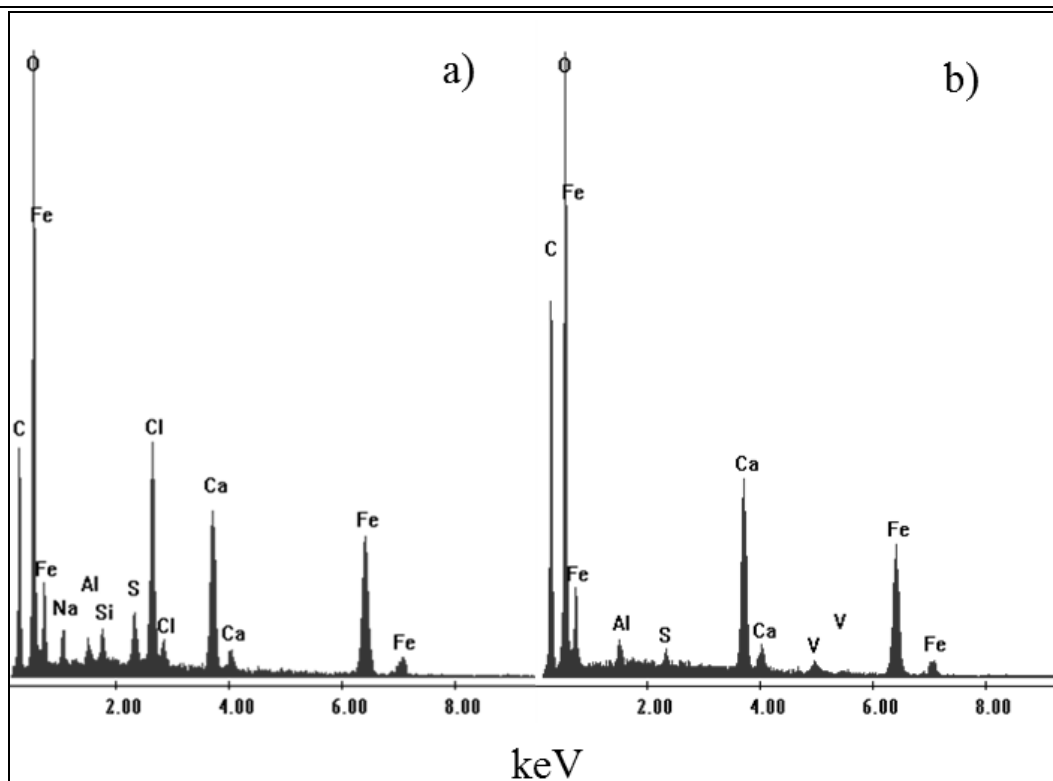


Figure 2. EDAX Images of a) Ca-Fe(III) alginate beads and b) Ca-Fe(III) alginate beads adsorbed with vanadium ions

Table 3. LC-ICPMS Speciation Analytical Method

LC	Agilent 1100
Analytical Colum	C ₁₈
Mobile Phase	EDTA 2.5mM, TBAOH 10mM, AC 60mM, (NH ₄) ₂ HPO ₄ 10mM at pH 6.73
Flow Rate	0.80 mL/min
Injection Volume	80 µL
ICPMS	Agilent 7500
RF power	1,500 W
Plasma gas flow rate	0.9 L/min
Nebulizer gas flow rate	0.16 L/min
Nebulizer pump rate	0.3 rps
Time per analysis	12 min

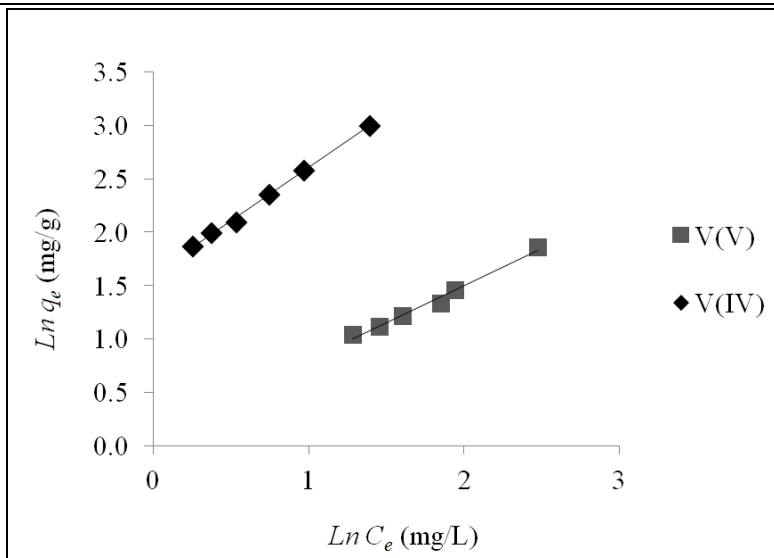


Figure 3. Freundlich isotherms for vanadium ions using 5 g/L of Ca-Fe(III) alginate beads at pH 6. 0.

Table 4. Desorption of vanadium ions using 0.1M of nitric, hydrochloric and sulfuric acid

	V(IV)		V(V)	
	% Desorbed	SD	% Desorbed	SD
0.1M HNO₃	90.0	10.8	100.0	0.0
HCl	95.9	1.3	100.0	0.0
H₂SO₄	91.1	2.8	100.0	0.0

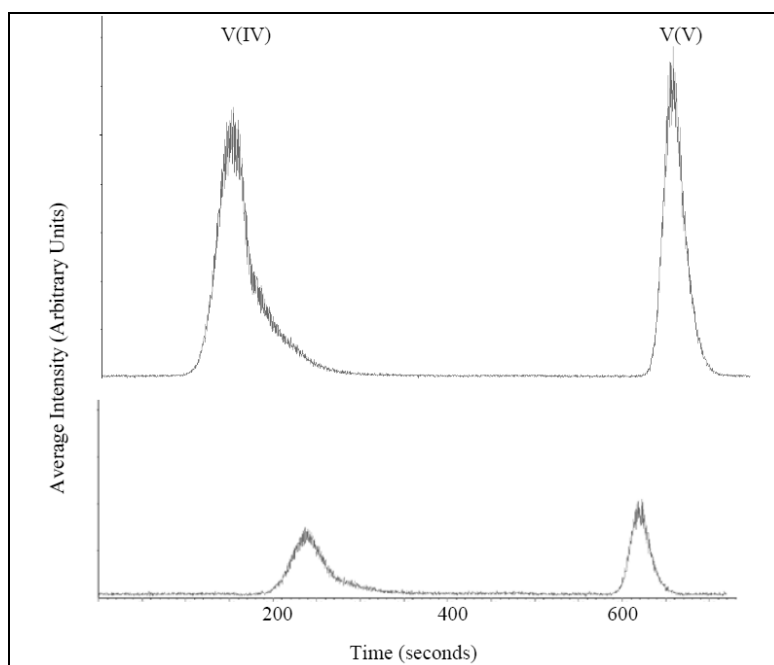


Figure 4. IP-ICPMS chromatogram of 150 µg/L vanadium inorganic species in solution after contact with 5g/L Ca-Fe(III) alginate beads at pH 6.0 a) 0.0 hrs contact b) 2 hrs contact

Table 5. Desorption of calcium and iron from Ca-Fe(III) during the desorption process of vanadium ions

	V(IV)		V(V)	
	% Ca Desorbed ± SD	% Fe Desorbed ± SD	% Ca Desorbed ± SD	% Fe Desorbed ± SD
HNO ₃	68.8±6.3	19.9±1.8	70.7±6.5	20.4±1.8
HCl	71.9±2.5	28.8±0.1	72.8±2.5	29.1±0.1
H ₂ SO ₄	72.2±1.0	46.5±3.7	73.6±1.0	47.4±3.7

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