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## Treatment of acidic mine drainage in an adsorption process using calcium silicate modified with Fe(III)



Kamila Barrera<sup>a</sup>, Alejandro Briso<sup>a</sup>, Viviana Ide<sup>a</sup>, Leonardo Martorana<sup>a</sup>, Gonzalo Montes<sup>b</sup>, Carlos Basualto<sup>a</sup>, Thomas Borrmann<sup>c</sup>, Fernando Valenzuela<sup>a,\*</sup>

<sup>a</sup> Unit Operations Laboratory, Faculty of Chemical and Pharmaceutical Sciences, Universidad de Chile, Santos Dumont 964, Independencia, Santiago, Chile

<sup>b</sup> Minerals and Metals Characterisation and Separation (M2SC) Research Group, Department of Mine Engineering Faculty of Physical and Mathematical Sciences, Universidad de Chile, Av. Tupper 2069, Santiago, Chile

<sup>c</sup> School of Chemical and Physical Sciences, Victoria University of Wellington, P.O. Box 600, 6140 Wellington, New Zealand

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### ABSTRACT

Two compounds based on calcium silicate hydrate and modified with Fe(III), using FeCl<sub>3</sub> and Fe(OH)<sub>3</sub> as iron sources, were synthesized, characterized and evaluated as adsorbents for removing ionic species from an arsenic-containing acidic aqueous mine solution. The adsorbents were prepared by contacting an aqueous solution of sodium silicate with calcium hydroxide and Fe(III) compounds. The structure of these adsorbents was determined by X-ray diffraction, FTIR, DSC, BET porosimetry analysis, mean particle size measurements and chemical analysis. Both adsorbents are amorphous, consisting of large agglomerates of particles whose mean particle size averages 358 nm with a surface area variable between 80 and 150 m<sup>2</sup>/g. Both adsorbents showed very similar fast adsorption behavior, achieving an almost quantitative and simultaneous uptake of arsenate, phosphate, Cu(II), Zn(II) and Cd(II) ions. In the pH range between 2 and 4, it was measured a maximum arsenic and phosphate loading capacities close to 55 mg As(V)/g of adsorbent and 81 mg phosphate/g adsorbent. Adsorption efficiencies over 99.94% were determined for the three metallic ions studied. The latter allowed the raffinate to comply with the limits accepted by environmental national regulation for ions discharging in natural water bodies. Particularly, As(V) equilibrium and kinetics were established in adsorption experiments. The hybrid Redlich-Peterson adsorption isotherm model explained the experimental results and a pseudo-second-order kinetic model provided a good fit to the experimental data. The modification with Fe(III) of the nano-structured calcium silicate generated a suitable adsorbent for removing arsenic species by forming highly insoluble and very stable double iron and calcium arsenate salts, keeping its ability to uptake other contaminants commonly present in acidic mine waters.

### 1. Introduction

This study addresses one of the most serious environmental problems in many mining countries, which is the generation of residual acidic aqueous solutions and the generation of acidic mine drainage (AMD) (Johnson and Hallberg, 2005). AMDs usually have a high SO<sub>4</sub><sup>2-</sup> ion content, variable toxic species, dissolved metals, and a high amount of colloidal-type suspended fine solids that have difficulty in settling (Matlock et al., 2002).

A typical AMD as found in Chile contains between 0.5 and 10 g/L of sulfate ions, has a pH-value between 0 and 4, and contains variable amounts of heavy metals up to 30–100 mg/L of Cu(II), Zn(II) and total Fe, [Fe(II) + Fe(III)]. Other species are also present, such as arsenates,

phosphates and other compounds, depending on the mineral deposit. The levels of these compounds regularly exceed the national environmental regulations for discharge of toxic elements, such as arsenic, present as As(V), Cd(II) and Pb(II), into continental water bodies. The metals remain in solution until the pH rises to a level where precipitation occurs. Chemical precipitation with lime or limestone poses many problems, such as re-dissolving metal precipitates, the need for a huge amount of chemicals, and the generation of a large volume of sludge. Furthermore, precipitation with CaO also offers incomplete sulfate and arsenate removal and fails to eliminate traces of other problematic contaminants.

Considering that chemical precipitation methods are far from being ideal approaches, over the last few years, several other techniques have

\* Corresponding author at: Laboratorio de Operaciones Unitarias, Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, Av.Santos Dumont 964, Independencia, Santiago, Chile.

E-mail address: [fvalenzu@uchile.cl](mailto:fvalenzu@uchile.cl) (F. Valenzuela).

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been developed and tested to reduce the amount of ionic pollutants from aqueous solutions, including ion-exchange (IX) with solid resins, solvent extraction (SX), chelation, oxidation and reduction, and biological treatments; all of these present advantages and shortcomings.

Undoubtedly, one of the most promising alternatives for the removal of ionic pollutants from acidic aqueous solutions are adsorption methods due to their simplicity of use and availability of many different types of natural and synthetic adsorbents. Most likely, the most common adsorbent used for water treatment is activated carbon (Julcour-Lebigue et al., 2012). Many other alternatives have been investigated, including zeolites (Yang et al., 2014), clays (Lee et al., 2011), and organic compounds such as chitosan (Negm et al., 2015). Many of these adsorbents have very different properties and adsorption capabilities, but their applicability is limited by cost and being impractical and/or uneconomical, which precludes in their implementation into industrial applications.

In general, inorganic adsorbents are more convenient than biological agents because of their stability in highly acidic oxidizing environments. This stability is due to their chemical composition and structure. Among them, metal oxides have been studied extensively as adsorbents, including  $\text{MnO}_2$ ,  $\text{ZrO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CuO}$  and  $\text{TiO}_2$ . However, their use is limited, as they are sensitive to many variables, including the pH and the ionic strength of the aqueous solution, the concentration of the adsorbate in the aqueous phase, the adsorbent particle size and its surface area. Normally, they are incapable of adsorbing cations and anions simultaneously. Furthermore, it is often very complicated to separate the spent metal oxides loaded with contaminants from the raffinate solution due to their small particle size and colloidal characteristics. In past years, several research groups have investigated the use of nano-adsorbents and functionalized nano-structured compounds in the treatment of aqueous solutions, where the concentration of some contaminants is normally low (Basualto et al., 2015; Mahmoud et al., 2015).

In this communication, it is described the synthesis, characterization and application of calcium silicate hydrates modified with Fe(III) to be used as adsorbent for removing contaminants from acidic aqueous solutions. These adsorbents were designed to have the capability to simultaneously uptake cation and anion species from acidic aqueous mine solutions. The adsorption mechanisms were studied and linked to their high surface area and chemical structure. In previous studies, it was synthesized a nano-structured calcium silicate hydrate (NanoCSH), which was used as the adsorbent in preliminary experiments for removing some heavy metals and anions from acidic solutions (Cairns et al., 2006; Valenzuela et al., 2013). Lately, attempts for modifying the surface of NanoCSH by introducing other metal atoms that generate improved adsorbents into their structure have been done. Modifications are aimed at producing more insoluble, stable and inert compounds easier to collect and dispose after the adsorption process. In this work, NanoCSH has been modified by partial replacement of Ca content with Fe(III) using  $\text{FeCl}_3$  and  $\text{Fe}(\text{OH})_3$  as sources of trivalent iron. This modification specifically aimed at improving the uptake of As(V) species from copper mine acid aqueous solution by producing very insoluble and stable double calcium and iron arsenates while retaining the proven adsorption capability of NanoCSH for removing metallic ions. The content of arsenic species in copper mine wastewaters varies from few to hundreds of mg/L. The concentration of arsenic species depends on the copper ore and its associated components, such as arsenopyrite and copper-arsenic bearing the minerals enargite and tennantite. Thereby, the adsorbent material could act as a pretreatment of further processes that decreases metalloid concentrations in water below the Chilean environmental regulations of discharge (Norm, 2001). As(V) adsorption equilibrium and kinetic information deduced from the experimental results are also discussed.

## 2. Experimental procedure

### 2.1. Synthesis of the adsorbent

The synthesis of calcium silicate hydrate (NanoCSH) modified with Fe(III) was conducted following a slightly modified procedure with respect to the one employed in the preparation of a non-modified NanoCSH used in previous studies (Valenzuela et al., 2013). The modification was achieved by replacing some amounts of calcium atoms of the silicate by iron atoms using  $\text{FeCl}_3$  and  $\text{Fe}(\text{OH})_3$  as Fe sources. Both Fe(III) compounds were tested with the aim of comparing the resulting products, termed FeNanoCSH, and identifying an effective modification process. Iron hydroxide was prepared from NaOH and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  as starting materials. The product was obtained by the chemical reaction between sodium silicate solution,  $\text{Ca}(\text{OH})_2$  and the iron compound at room temperature in a two-step procedure. In the first step,  $\text{FeCl}_3$  or  $\text{Fe}(\text{OH})_3$  were added to a suspension of  $\text{Ca}(\text{OH})_2$  in water; then, this mixture was treated with a concentrated HCl solution under vigorous stirring at a velocity of approximately  $1000 \text{ min}^{-1}$ . Second, sodium silicate solution was vigorously mixed into the previously prepared  $\text{Ca}(\text{OH})_2$ -Fe suspension in a batch reactor, keeping a stirring velocity between 1000 and  $2000 \text{ min}^{-1}$ . A precipitate corresponding to a calcium silicate hydrate modified with iron (FeNanoCSH) formed rapidly. The precipitate was allowed to settle for 12–15 h before the solids were collected by vacuum filtration. The solid material was washed with water and ethanol to maintain the integrity of the structure and its active surface area. Finally, the solid adsorbent was dried at 358 K for 24 h. To establish the optimal level of Fe modification, several experimental runs were carried out varying the molar quantity of Ca replaced by Fe in a range between 5 and 50 M% and attempting to maintain the nano-structure of the base NanoCSH, which is associated with wollastonite ( $\text{CaSiO}_3$ ) and silicate hydrates.

### 2.2. Characterization of the adsorbent

The adsorbent FeNanoCSH was characterized using different methodologies. To determine the crystalline or amorphous character of the adsorbent, samples of the solid particles were analyzed using X-ray powder diffraction in a BRUKER D8 ADVANCE device. The morphology of the adsorbent particles was observed by scanning electron microscopy (SEM) using a JEOL JSM-25SII instrument. The mean particle size was measured using dynamic light scattering (DLS) in a Malvern Mastersizer Hydro 2000 MU apparatus. In addition, analysis of porosimetry, including the determination of the surface area of the particles, was determined by BET measurements using a  $\text{N}_2$  sorptometer at 77 K in a Micrometrics ASAP 2010 device. Infrared spectra of calcium silicate modified with iron were obtained by mixing and grinding the solid adsorbent with KBr for measurement in a Bruker-FTIR IFS 55 instrument in the range  $400\text{--}4000 \text{ cm}^{-1}$ . Differential Scanning Calorimetry (DSC) measurements of the adsorbent were conducted under inert atmosphere using a DSC Perkin Elmer 6000 instrument limited to the  $0\text{--}400 \text{ }^\circ\text{C}$  range. The content of Si was determined by elemental analysis. In addition, the content of Ca and Fe in the adsorbent was also measured by flame atomic absorption analysis using a Perkin Elmer PinAAcle 900F apparatus, a technique that was also used to check the chemical stability of the adsorbent when in contact with acidic aqueous solutions; these are necessary tests that take the acidic nature of most mine wastewaters into account.

### 2.3. Adsorption studies

The first experiments were designed to check the chemical stability of the adsorbents when in contact with acidic aqueous solutions. Equilibrium experiments were carried out to determine the adsorption capacity of FeNanoCSH. Particularly, the adsorbent loading capacities for removing Cu(II), Zn(II), Cd(II), arsenic as arsenate and phosphate

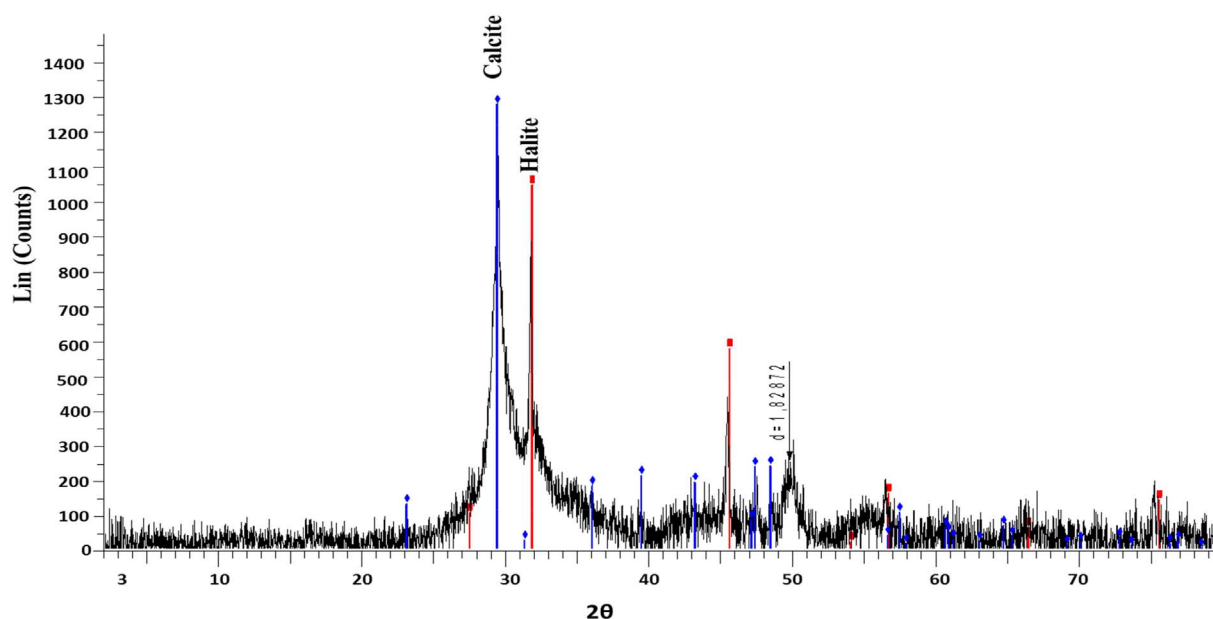


Fig. 1. X-ray diffraction analysis of FeNanoCSH replacing 10 M% of Ca by Fe.

ions were measured. Adsorption experiments were repeated several times at 298 K in a Polyscience orbital-shaker apparatus by contacting the synthesized adsorbent with samples of a modified acidic mine aqueous solution, with an average composition of 108 mg/L Cu(II), 60 mg/L Zn(II), 25 mg/L Cd(II) and variable contents of arsenate,  $\text{PO}_4^{3-}$  and sulfate ions. The acidity of the solution was adjusted to be in the range between pH 2.0 and 5.0.

A set of arsenic adsorption equilibrium and kinetics experiments were also performed at the same temperature. The batch experiments were conducted over sufficient time to attain equilibrium. Kinetics experiments were conducted by measuring the change of the contaminant species in the aqueous feed solution as a function of time. In all of the adsorption experiments, once the time had elapsed, the suspension was filtered through a 0.45  $\mu\text{m}$  nitrocellulose Millipore membrane in order to determine the concentration of the ionic species in the raffinate. The amount of ions adsorbed onto FeNanoCSH was calculated from the mass balance between the initial and final concentrations of the ionic species in the aqueous solution.

The measurement of metal ion and arsenic concentrations in all acidic aqueous solutions was measured by the atomic absorption spectrophotometry method using the Perkin Elmer PinAAcle 900F apparatus. When necessary, ICP-MS was used for determining lower concentrations of ions dissolved in solutions. Phosphate ion concentrations were measured using the vanadate-molybdate-phosphoric UV-spectroscopy method (Norm, 2009).

### 3. Results and discussion

#### 3.1. Synthesis and characterization of the adsorbents

The yields of the syntheses were high, and the reaction was very efficient and reproducible. The reaction of Ca(II) ions with soluble silicate and Fe(III) produced precipitates that formed rapidly and were very insoluble and amorphous. The obtained solids were thixotropic, indicating agglomeration of the particles (Iler, 1979). Borrmann et al., based on spectroscopic analysis, proposed a structure for this sort of adsorbent composed of a backbone of silicates with plates approximately 2 to 10 nm thick made of repeat units of approximately 5 silicate tetrahedrals with calcium ions and silanol groups on the surface, which would act as binding or nucleation sites (Cairns et al., 2006). These characteristics also apply to the compounds synthesized in this work.

This information confirms that the adsorbents prepared in this study are nano-structured, although they can be classified as microadsorbents.

The use of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  resulted in better products than when using  $\text{Fe}(\text{OH})_3$ . Iron chloride based compounds were impalpable orange-red-brownish colored solids in which Fe appeared to be dispersed evenly throughout the silicate structure. In addition, only a certain amount calcium could be effectively replaced by Fe(III) ions and result in a high surface area product, approximately 13%. When a higher Fe molar % was used for producing the modified adsorbent, a hard and brittle solid was obtained, which had a lower adsorption capacity towards the diverse ionic species studied in this work. The excess of iron during the synthesis would tend to form  $\text{Fe}(\text{OH})_3$  on the surface of the silicate structure and not integrate into it, thereby compromising the formation of the base and repeat units. During the synthesis of the adsorbent, a number of different synthetic products can be expected. Several reactions occur in parallel, given that the source of silicate species was a mixture; sodium silicate solutions typically contain oligomers of silicate and silica with various chain lengths along with sodium ions. If an additional species, such as Fe(III), is entered into the reaction of this mixture of silica and silicates with calcium hydroxide, it is likely that the resulting modified nano-structured silicate will have even more variety in its functional groups, such as surface iron and calcium, hydroxyl and silanol groups, and in its base and repeat units. This fact makes it difficult to estimate a synthesis yield for the chemical reactions carried out and raises the importance of establishing the bulk properties of the adsorbents and the determination of their adsorption capacities.

Fig. 1 presents the XRD pattern of FeNanoCSH prepared by replacing 10 M% of calcium by  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ . Powder X-ray diffraction (XRD) analysis showed that all FeNanoCSH adsorbents synthesized were amorphous. The structure of the silicate would be related to the mineral species wollastonite, which is a natural crystalline salt; however, NanoCSH tends to be amorphous given the diverse mix of silicate and silica species present in the sodium silicate solution. The presence of Fe species was not observed due to the low proportion of iron in the modified amorphous silicate.

Fig. 2 shows SEM micrographs of the synthesized silicates. Fig. 2a is the image of an unmodified nano-structured calcium silicate, and Fig. 2b is the image of an iron-modified FeNanoCSH. The images confirmed the amorphous character of FeNanoCSH adsorbents. The formation of agglomerates of particles without a particular structure was also observed.

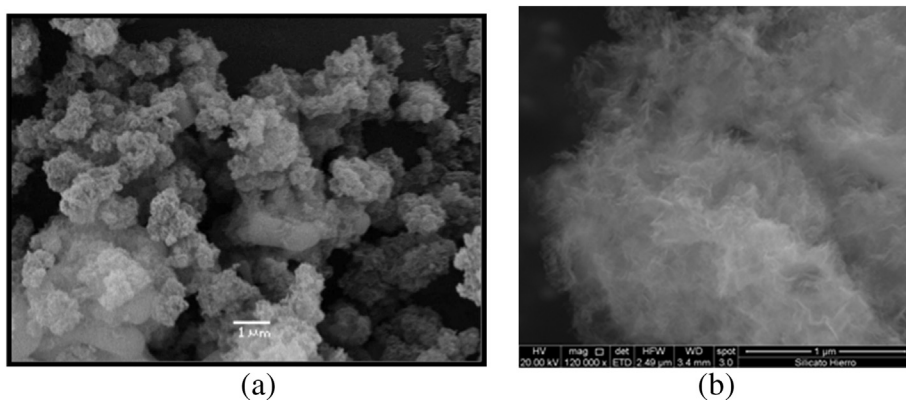


Fig. 2. SEM images of the adsorbent, unmodified NanoCSH (a) and FeNanoCSH (b).

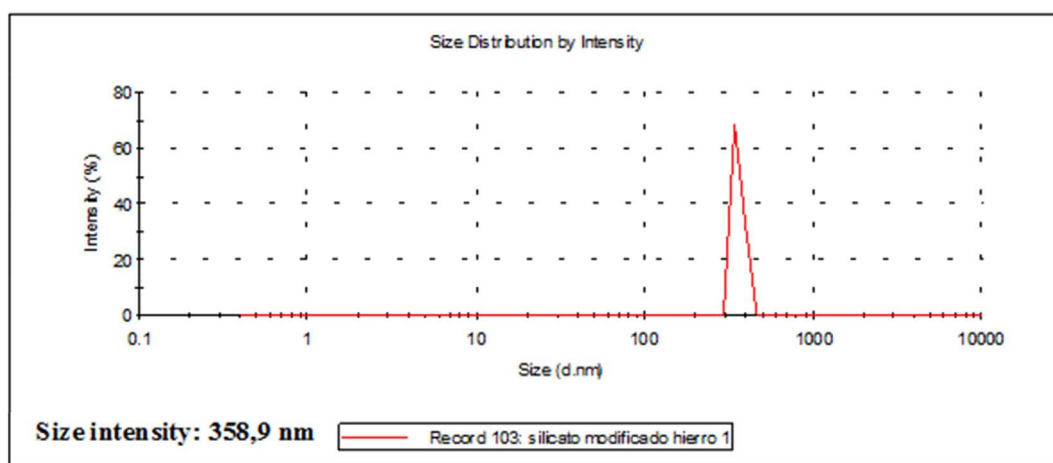


Fig. 3. Size particle distribution of the adsorbent modified with Fe(III).

Fig. 3 shows the particle size of the adsorbent, which was determined using the Malvern Mastersizer apparatus. The mean particle size was 300 to 500 nm, with an average size of approximately 358.9 nm. It should be noted that the sizes recorded depended on the stirring speed employed during the synthesis.

Porosimetry analysis measurements of FeNanoCSH were conducted using a  $N_2$  sorptometer at 77 K. An average surface area between 78 and  $149 \text{ m}^2/\text{g}$  was measured for the adsorbents. The surface area also depended on the stirring speed during the synthesis of the silicate. The surface areas measured for the FeNanoCSH adsorbents were somewhat smaller than those obtained for NanoCSH but were considered sufficient to produce compounds showing efficient adsorption capacities and kinetics. A mean pore diameter between 10 and 20 nm and a pore volume between of 0.24 and  $0.43 \text{ cm}^3/\text{g}$  were calculated from the measurements. The nano-structure of FeNanoCSH is considered to be comprised of a great many vacant adsorption sites distributed on the external and, more importantly, on the accessible internal surface area of FeNanoCSH in a three-dimensional hierarchical structured material. The accessibility of the internal surface is confirmed by the  $N_2$  adsorption-desorption isotherms. These curves (shown in Fig. 4) indicate the filling of micropores at a low relative pressure and of mesopores at pressures between 0.2 and 0.7 ( $P/P_0$ ). Both type of pores are associated with the internal structure of the iron-modified silicate. The hysteresis curves also show that the macropores formed around aggregated particles at higher relative pressures (Huang et al., 2010). The shape of the hysteresis loop indicates a Type C pore structure, meaning that the pores are wedge-shaped opening to the outside. From the measurements, it was not clear if the pores reach all the way through the particles or form pockets. What could be deduced was that the FeNanoCSH structure would allow an efficient adsorption process due to its accessibility.

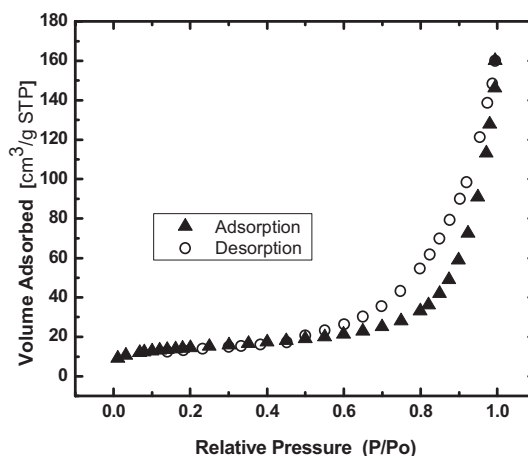
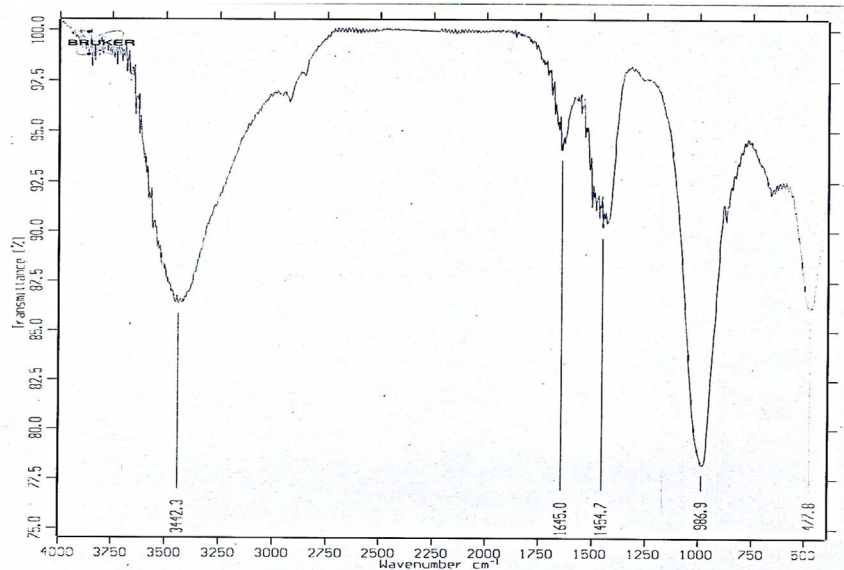


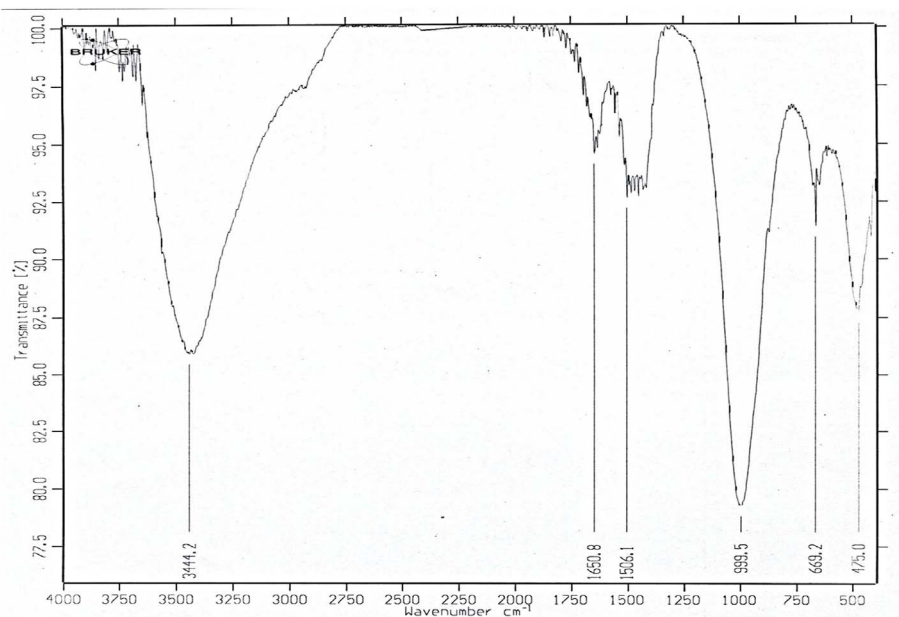
Fig. 4. Nitrogen adsorption-desorption isotherms of FeNanoCSH.

Fig. 5 corresponds to the FTIR spectra of FeNanoCSH formed from  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (Fig. 5a) and  $\text{Fe}(\text{OH})_3$  (Fig. 5b), respectively. Both spectra are very similar, showing, in both cases, a broad band at approximately  $3440 \text{ cm}^{-1}$  assigned to free water molecules, sharp bands at approximately  $1645\text{--}1650 \text{ cm}^{-1}$ , which are very probably O–H bending bands associated with water and silanol groups (Nakamoto, 1978). Both spectra also showed an intense band at approximately  $1000 \text{ cm}^{-1}$  due to the symmetric and antisymmetric stretching of Si–O bonds within the tetrahedral groups as well as another band at approximately  $480 \text{ cm}^{-1}$ , which was interpreted as symmetric and antisymmetric bending of the O–Si–O bonds (Fernández-Carrasco et al., 2012). Ca–O and Fe–O bands appear at lower frequencies and were not recorded.





(a)

Fig. 5. Infrared spectra of FeNanoCSH synthesized using  $\text{FeCl}_3$  (a) and  $\text{Fe}(\text{OH})_3$  (b).

(b)

Differential scanning calorimetry analysis (DSC) measurements of FeNanoCSH are shown in Fig. 6. The existence of an endothermic peak in the DSC curve at 92–94 °C was associated with the loss of free water molecules from the hydrate adsorbent. At approximately 350 °C, another endothermic peak was observed, which reflects the internal dehydration of the iron and calcium silicate (El-Naggar and Abou-Mesalam, 2007).

Additionally, the contents of Ca and Fe in both FeNanoCSH adsorbents were determined using a conventional acid-dissolution method followed by flame atomic absorption analysis. A chemical analysis FeNanoCSH, where 13 M% of Ca was substituted by Fe, indicated the average presence of 27.95% (w/w) Ca and 6.18% (w/w) Fe in the adsorbent. These values were consistent with the extent to which calcium atoms were replaced by iron atoms during the synthesis. Furthermore, a content of Si variable between 18.9% (w/w) and 22.2% (w/w) was determined in the solid. The difference corresponds to the content of water molecules associated with the silicate.

### 3.2. Adsorption experiments

#### 3.2.1. Adsorption of ionic species

Both FeNanoCSH adsorbents were highly stable in solutions within the pH range between 2.0 and 6.0 and performed, in this respect, far better than the unmodified NanoCSH. It is possible that the presence of Fe atoms gave the calcium silicate a more rigid structure, generating greater chemical inertia. It is known that the chemical stability of multi-component compounds can be superior to single salts.

A set of experiments were designed to measure the ability of FeNanoCSH to remove arsenate and phosphate anions and the metallic ions Cu(II), Zn(II) and Cd(II) from the mine acidic aqueous solutions with compositions as described above. However, in order to establish the maximum metal adsorption capacity of these adsorbents, some experiments were carried out using laboratory-generated feed aqueous solutions in which the content of the ionic species was increased to higher values than those found in the naturally occurring mining waste

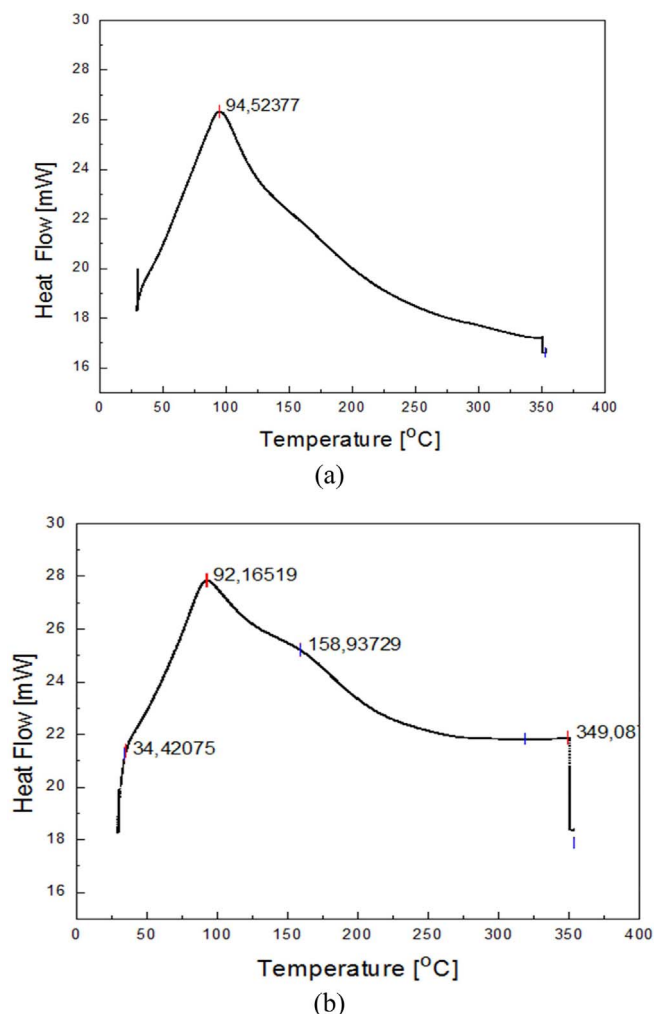


Fig. 6. DSC analysis of FeNanoCSH synthesized using FeCl<sub>3</sub> (a) and Fe(OH)<sub>3</sub> (b).

fluids. For all adsorption experiments, the choice of adsorbent was based on the results of the synthesis experiments designed to modify NanoCSH and establishing the maximum feasible content of Fe in the composite. Consequently, FeNanoCSH with a 13 M% replacement of Ca for Fe were used as adsorbents. The results for FeNanoCSH produced from the two different iron sources were compared.

The uptake of As(V) for the acidic solution as AsO<sub>4</sub><sup>3-</sup> ions was studied. To gain insights into the adsorption ability of the adsorbents, the adsorption parameters were varied, such as the initial pH of the aqueous solution, the mass of adsorbent and the effect of the initial concentration of arsenates in the mine water.

The results of varying the pH value are shown in Fig. 7. These experiments were conducted using an aqueous solution with a As(V) concentration adjusted to a value of 50 mg/L and 200 mg of the adsorbents used.

In this figure, the disappearance of arsenic from the aqueous solution  $C_t/C_o$  is plotted as a function of pH, where  $C_t$  and  $C_o$  denote this metalloid content at time  $t$  and its initial concentration, respectively. Two insights were obtained from the results. The adsorption responses of both FeNanoCSH compounds were very similar overall. The adsorption capacity for FeCl<sub>3</sub>-based FeNanoCSH was 6.01 mg As(V)/g adsorbent and 5.88 mg As(V)/g FeNanoCSH based on iron hydroxide. The FeNanoCSH based on iron chloride was slightly more efficient than the FeNanoCSH based on iron hydroxide. The second insight was that, for both adsorbents, the uptake tended to be nearly independent of the initial acidity of the aqueous solution in the studied range within the margin of error. Although it is well-known that the acidity of an

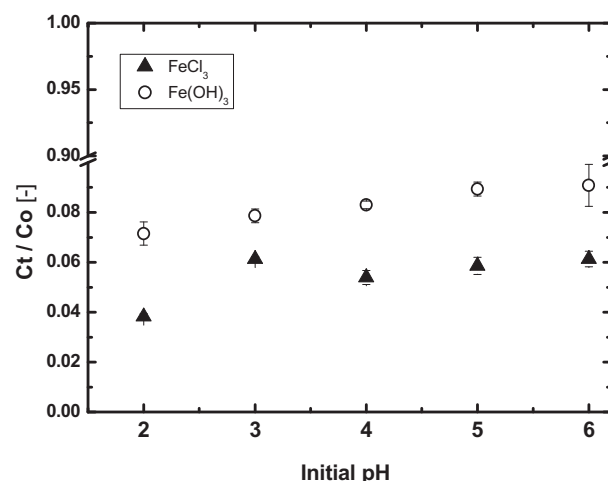


Fig. 7. Dependence of As(V) removal on the initial pH of the aqueous solution.

aqueous solution can strongly affect the surface properties of the adsorbent and the adsorbing capacity of the adsorbates, these results showed that, within the pH range used, a comparatively high adsorption was achieved, independent of pH, with very minor variations. A minor trend towards a better performance at pH 2 than at pH 6 was observed. However, due to the margin of error of the measurements, this trend should be treated with caution. Measurements at pH values below 2.0 were not carried out, as the arsenate ions are totally protonated (H<sub>3</sub>AsO<sub>4</sub>) below this value, which is known to significantly change their adsorption behavior in a negative way. Furthermore, under such acidic conditions, excess H<sup>+</sup> ions would compete with the contaminant ions for the adsorption sites and most likely render the sorbent ineffective. After the adsorption, the pH values of the raffinate were measured. In all cases, strong alkalization of the resulting residual aqueous solutions occurred with the pH values ending up in the range of 9 up to 11. This fact indicates that FeNanoCSH acted as a buffer, keeping the pH stabilized in the basic region and generating very stable precipitates, which should be easier to separate from the raffinate solutions compared with those obtained when lime, NaOH or soda ash are used as precipitant. The removal of arsenate species is explained by the formation of insoluble calcium arsenate Ca<sub>3</sub>(AsO<sub>4</sub>)<sub>2</sub> and calcium iron arsenate (Ca)<sub>3</sub>(Fe)(AsO<sub>4</sub>)<sub>3</sub>. Values of solubility product constants at 25 °C of 6.8·10<sup>-19</sup> and 5.8·10<sup>-21</sup> are reported in the literature for calcium arsenate and iron arsenate, respectively (Freiser and Freiser, 1992). Effectively, the presence of iron in the formation of calcium arsenates leads to the production of more insoluble and chemically and physically stable precipitates than those observed in prior studies, which is the central purpose of this work. Considering the abundance of iron and calcium in mining tailings, the species produced are appropriate for disposal, for example, in mining tailing dams. In Chile, there have been prior research efforts for producing exactly these compounds and locking arsenic up in them in mining tailings. These efforts focused on using lime and iron compounds in a process that was not always complete or efficient. These compounds were generated directly on the FeNanoCSH adsorbent, making FeNanoCSH highly desirable for the long-term remediation of arsenic pollution. Furthermore, FeNanoCSH is produced using low-cost raw materials, such as Ca(OH)<sub>2</sub> and sodium silicate solution, which is a very common industrial substrate produced in Chile from waste glass.

The dependence of the As(V) adsorption on the mass of adsorbent employed in the experiments is shown in Fig. 8. An aqueous solution was used with an initial pH adjusted to a value of 2.0 and an arsenic concentration of 50 mg/L. Both adsorbents showed very similar adsorption behavior and that the adsorption of As(V), at a constant amount of As, was dependent on the mass of the adsorbent up to a saturation level of approximately 200 mg. Obviously, a larger amount

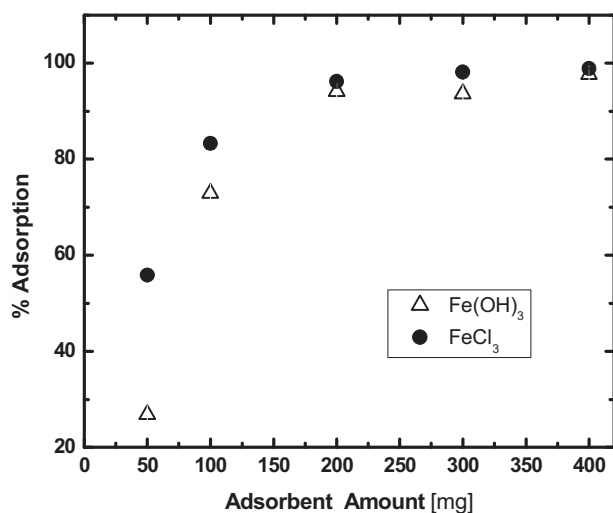


Fig. 8. Effect of the mass of adsorbent on As(V) removal.

of adsorbent offered a larger amount of available active adsorption sites and a higher surface area for the process. However, if all the vacant sites are filled and saturated by the ions to be removed, adding more adsorbent does not change the adsorption maximum, as shown in Fig. 8.

These experiments lead us to design another set of adsorption procedures with the purpose of obtaining the maximum As(V) loading capacity for both FeNanoCSH adsorbents. Given the number of active adsorption sites that the adsorbent could present in its structure and the presence of calcium and iron atoms, it is possible to determine an optimum relationship between the concentration and volume of arsenic-containing solution and the suitable mass of adsorbent to employ. The effect of the initial As(V) content in relation to the adsorption capacity or arsenic-loading capacity of both adsorbents “*q*” expressed in mg As/g adsorbent is presented in Fig. 9. These experiments were conducted using a modified mine aqueous solution with an initial pH of 2.0 and 200 mg of the silicated adsorbent.

Both FeNanoCSH adsorbents at this pH adsorbed a very similar amount of arsenic as a function of the initial concentration of the ion in the aqueous solution. The experimental results reached a plateau at a *q* value of 55 mg As per g of adsorbent and approximately 530 mg of As (V) per L. This indicated that, using the adequate ratio of metal content in the aqueous solution to the quantity of adsorbent, it was possible to achieve arsenic loading capacities close to 55 mg As(V)/g of adsorbent,

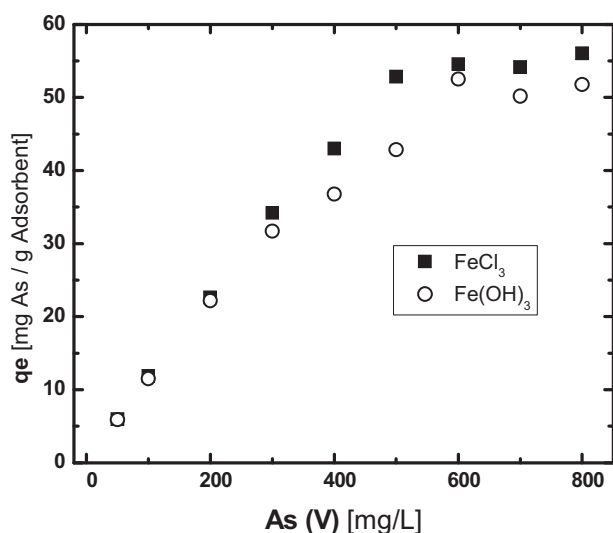


Fig. 9. Effect of the initial concentration of As(V) on the adsorption capabilities of FeNanoCSH adsorbents.

**Table 1**  
Removal of ionic species from the acid solution using nano-structured calcium silicate modified with FeCl<sub>3</sub>.

Species	Initial concentration (mg/L)	Raffinate concentration (mg/L)	Loading capacity, “ <i>q</i> ” (mg species/g adsorbent)	Adsorption extent (%)
Cu(II)	108.2	0.056	13.51	99.94
Cd(II)	25.1	0.004	3.14	99.98
Zn(II)	59.8	0.005	7.47	99.99
PO <sub>4</sub> <sup>3-</sup>	311.0	1.090	38.75	99.65

which is a very high value for a natural acidic solution, similar to or higher than the arsenic loading capacity measured for other conventional adsorbents (Mohan and Pittman, 2007). However, it is not easy to compare adsorption capacities to values in the literature, which have been evaluated under different experimental conditions.

Additional adsorption experiments were conducted in order to measure the capability of the nano-structured calcium silicate modified with iron towards Cu(II), Zn(II), Cd(II) and phosphate ions, all present in the studied aqueous solution. These ions are commonly present in acidic mining waste solutions associated with metal sulfide and phosphate rock deposits. Based on the slightly better performance of the iron chloride-based FeNanoCSH, the experiments for these tests all employed this FeNanoCSH. The experiments were carried out using the acidic copper mine water containing approximately 108.2 mg/L Cu(II), 59.8 mg/L Zn(II), and 25.1 mg/L Cd(II) as well as an initial content of phosphate anion of 311 mg/L at an initial pH value of 2.0. The experiments were carried out by contacting 200 mg of the adsorbent with 25 mL of aqueous feed solution in each trial. The results are presented in Table 1 for each of the ionic species.

Table 1 indicates the almost complete removal, within the detection limit, of all studied species within a few minutes. The uptake of copper, cadmium, zinc and phosphate reached adsorption rates of over 99.9% in all cases. The metallic ions were removed by a combined mechanism of forming the respective hydroxide or mixed hydroxides with phosphate, sulfate and silanol groups of silicates via cation exchange of the calcium and iron atoms of the silicates. Effectively, the polysilanol groups act as a source of OH<sup>-</sup> ions by releasing them into the aqueous solution. Thus, they can act as binding sites for metal ions and also promote the formation of metal hydroxides by providing enough alkalinity for the precipitation of the corresponding species. By keeping the pH value above 9.0, FeNanoCSH produces very stable precipitates. In turn, calcium exchange would be favored due to the size of the hydrated Ca radii opening sites for the adsorption of metal ions with smaller radii. Interestingly, the three cations, Cu(II), Cd(II) and Zn(II), were all quantitatively extracted with little distinction despite the differences in their hydrated radii. Most likely, all of them would form very stable inner-sphere-type surface complexes under the experimental conditions, and the stability of the precipitates formed became more important than the size of the hydrated radii in solution.

Furthermore, all metal hydroxide species formed on the surface of the FeNanoCSH adsorbents and not as discrete hydroxide particles in solution, which made them easier to separate from the aqueous solution by settling or filtration because of the granular nature of the spent FeNanoCSH. This is an advantage compared to employing lime or NaOH... because these compounds often result in incomplete removal of most of metallic ions. They produce colloidal suspensions that tend to redissolve generating unstable sludges that are hard to recover and treat. Table 1 also indicates the ion loading capacities for this adsorbent measured under the experimental conditions used herein. These “*q*” values for a determined mass of adsorbent, are sensitive to the concentration of the metallic ions in aqueous solution and tend to achieve much higher values of metal loading capacity when greater concentrations of the metals are present in solution.

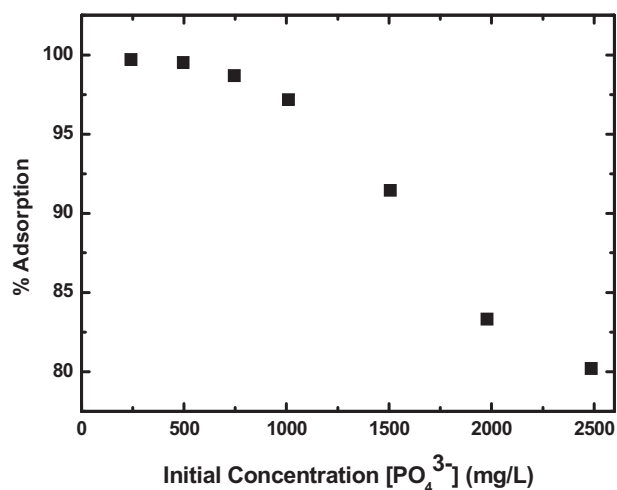


Fig. 10. Effect of the initial content of phosphate ions on their adsorption using FeNanoCSH.

Adsorption of phosphate anions was almost quantitative. Only a residual concentration of the anion of just 1.09 mg/L was detected when starting from an initial content of 311.0 mg/L, which represents an anion loading capacity of 38.7 mg phosphate/g adsorbent. Removal of this anion is explained by the formation of a very insoluble hydroxy apatite with calcium or by the formation of a calcium and iron phosphate salt that would be adsorbed on the surface of the modified calcium silicate. In general, the removal of anions, such as arsenate and phosphate ions, would be effectively based on the formation of calcium and calcium iron insoluble salts. Therefore, the formation of these species is associated with the release of calcium ions from the original silicate.

With the purpose of determining the maximum phosphate loading capacity of FeNanoCSH, several experiments were carried out with varying initial concentrations of phosphate in the range between 250 and 2500 mg/L and at a pH value of 4.0. The results of saturating the adsorbent in phosphate is shown in Fig. 10. A complete adsorption of this anion was achieved, even for a content of this anion in aqueous solution of approximately 500–650 mg/L, which gave a loading capacity between 62.5 and 81.3 mg phosphate/g adsorbent.

From all of the experimental results reported in this work, it is clear that this FeNanoCSH adsorbent has a huge adsorption capacity for removing the contents of several ionic species concurrently from the acidic solutions tested in this study. The adsorbent was easily and reproducibly prepared, which ensures its potential to be used to clean up a broad variety of acidic residual mining and industrial waste solutions. It has displayed important features that make it advantageous compared to other adsorbents due to the species formed on its surface. In this study, the uptake of sulfate was not monitored.

Sulfate will be the subject of a further study. It should be noted that its presence in the acidic solution did not affect the adsorption of the species reported in this study. Fine solid particles existing in the acid solution were not investigated closely, but it was noted that they were removed from the mining waters. They were likely trapped in the adsorbent structure due to the wedge-shaped pores. Clear raffinates were obtained after the adsorption processes using FeNanoCSH.

### 3.2.2. Adsorption equilibrium

From a practical point of view, it is necessary to get information about the adsorption equilibrium behavior of the FeNanoCSH adsorbent towards the different adsorbates. We have included in this study some experiments aimed at determining the relationship between the quantity of the As(V) ions adsorbed by FeNanoCSH under different experimental conditions. The adsorption equilibrium is usually described by some adsorption isotherms whose parameters express the surface

properties and the affinity of the adsorbent to the adsorbate at a given temperature and pH. Experimental results of equilibrium experiments were analyzed using the usual Langmuir, Freundlich and Redlich-Peterson isotherm models. The very well-known Langmuir isotherm represents a theoretical monolayer-type adsorption on a homogeneous surface. In turn, the Freundlich isotherm corresponds to an empirical model assuming a heterogeneous surface and several layers. The Langmuir isotherm showed good but not complete agreement with the experimentally observed values. In turn, the Freundlich isotherm model did not fit well to the experimental values. The experimental data were analyzed using the Redlich-Peterson isotherm, which is a hybrid adsorption model that incorporates characteristics of both Langmuir and Freundlich models according to the following equation (Ho et al., 2002):

$$q_e = \frac{A \cdot C_e}{1 + K_{R-P} C_e^{g_{R-P}}} \quad (1)$$

where  $q_e$  denotes the amount of As(V) adsorbed at equilibrium in  $mmol$  As(V)/g adsorbent and  $C_e$  is the concentration of this ion, in  $mmol/L$ , that remains in solution after the extraction.  $A$  (L/g) and  $K_{R-P}$  (L/mmol)<sup>g</sup> are Redlich–Peterson model constants.  $g_{R-P}$  [-] corresponds to the model exponent, whose value is theoretically limited between 0 (where it behaves as in Henry's law) and 1 (where it behaves as in the Langmuir isotherm).

Equilibrium experiments were carried out at 30 °C using samples of the same acidic solutions employed in the previous experiments, but the initial arsenic content was varied between 50 and 500 mg/L. All solutions had an initial pH value of 2.0. As before, solutions were filtered prior to experiments using Millipore membranes to avoid the presence of detrimental solid particles. The results for As(V) adsorption, using both FeNanoCSH based on FeCl<sub>3</sub> and Fe(OH)<sub>3</sub> in the treatment of acidic mine solutions, are shown in Fig. 11. In the figure, the amount of metal adsorbed,  $q_e$ , was plotted against the equilibrium metal concentration. The continuous line represents the values calculated by the model, according Eq. (1).

The parameters were evaluated by non-linear regression using the Lavenberg–Marquardt iteration routine. Instead of the R<sup>2</sup> values that are commonly used to evaluate linear models, in this non-linear case,  $\chi^2$  was calculated, which represents the error between the experimental data and the values obtained from the model (Ho, 2004). This approach is more appropriate for non-linear equations, with lower  $\chi^2$  values indicating better agreement. The values for the parameters of the Redlich-Peterson equilibrium adsorption model obtained for both adsorbents

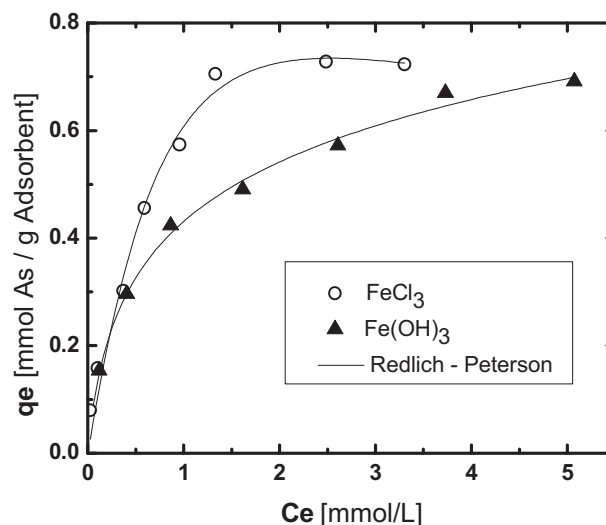


Fig. 11. Redlich-Peterson isotherms for As(V) adsorption onto nano-structured calcium silicate modified with FeCl<sub>3</sub> and Fe(OH)<sub>3</sub>.



**Table 2**  
Redlich-Peterson adsorption equilibrium isotherm model parameters.

	$K_{R-P}$ (L/mmol) <sup>g</sup>	$A$ (L/g)	$g_{R-P}$ [-]	$\chi^2$
FeCl <sub>3</sub>	1.04 ± 0.18	0.72	1.08	0.00166
Fe(OH) <sub>3</sub>	2.13 ± 0.49	3.95	0.79	0.09003

are given in Table 2. As Fig. 11 and the values determined for  $\chi^2$  (0.001–0.09 mmol/g) included in Table 2 show, this adsorption equilibrium model fits the experimental results well and was in better agreement than the other models studied.

The values of  $q_e$  calculated by this model (continuous lines) were in good agreement with those experimentally observed,  $q_{exp}$ . Furthermore,  $g_{R-P}$  values near 1.0, as shown in Table 2, indicated that the adsorption was closer to the Langmuir isotherm than Freundlich equation for this hybrid model, which is in agreement with our attempts to apply these models directly. This result indicated that, during the process, the active adsorption sites were permanently renewed, which indicates a process approaching an ideal Langmuir model. Based on the Langmuir isotherm, the dimensionless equilibrium parameter,  $R_L$ , associated with the intensity of the adsorption could be determined according to the following equation (Lewinsky, 2007):

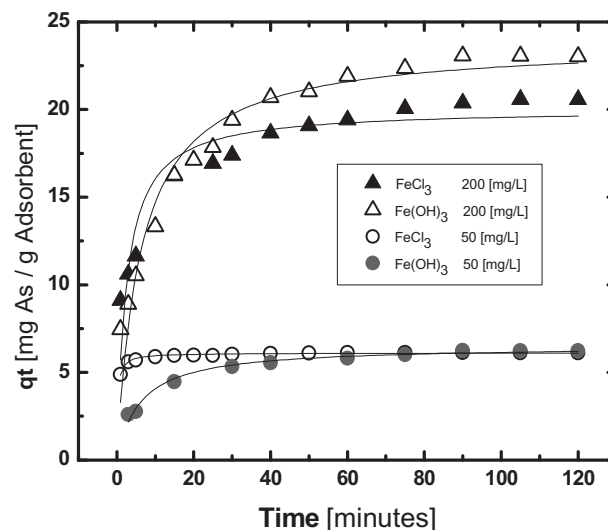
$$R_L = \frac{1}{1 + K_L \cdot C_0} \quad [-] \quad (2)$$

where  $K_L$  is the Langmuir constant and  $C_0$  is the initial concentration of arsenic (V) in aqueous solution in mmol/L. When the value of  $R_L$  is between 0 and 1, the adsorption is favorable; when  $R_L$  is close to 0, it is irreversible. Using the  $K_L$  calculated values from the Langmuir model in this study (1.505 L/mmol for Fe(OH)<sub>3</sub> and 1.857 L/mmol for FeCl<sub>3</sub>) and the range of concentrations of As(V) in solution, all calculated values of  $R_L$  were between 0 and 1, confirming that the adsorption of this ion on the surface of FeNanoCSH was always favorable. Furthermore, it was found that the higher the content of As(V) in aqueous solution was, the lower and closer to 0 the values of  $R_L$  were, indicating that the intensity of the adsorption was also higher and that irreversible adsorption processes occurred close to saturation.

### 3.2.3. Adsorption kinetics

To obtain information concerning the adsorption rate of As(V) ions from acidic solutions on FeNanoCSH, a set of kinetic experiments were carried out using samples of the acidic solution employed in the prior experiments with the average composition described above. However, for a better analysis of the results, the arsenic (V) content in solution in these experiments was adjusted to be between 50 mg/L and 200 mg/L with an initial pH of 3.0. Fig. 12 shows the results for both variations of FeNanoCSH. A fairly fast initial rate of adsorption was observed. The amount of As(V) ions adsorbed depended on the initial content of this metalloid in solution. During the initial stages of the adsorption process, a large number of vacant sites and reactive species were available, leading to a fast process with the number of adsorption sites being the driving force of the process. Conversely, as the adsorption process proceeded, the number of vacant sites diminished and deposits started to impede the diffusion of species to the silicate surface; hence, the uptake slowed down.

Many authors have proposed different adsorption rate models that explain the experimental results of using natural or synthetic adsorbents (Ho et al., 2002; Kumar and Sivanesan, 2005; Anirudhan and Radhakrishnan, 2008). In general, these models consider a mass transfer process accompanied by chemical reactions. These include the diffusion of the adsorbate from the free aqueous phase towards the outer surface of the adsorbent followed by a chemical reaction mechanism between the adsorbent and the adsorbate (Kamio et al., 2005). In this work it was applied to the experimental values to both a pseudo-first-order-kinetic model (Ho and McKay, 1998), which did not fit the



**Fig. 12.** Adsorption kinetic of As(V) on FeNanoCSH based on FeCl<sub>3</sub> and Fe(OH)<sub>3</sub>. Initial As(V) content: 50 and 200 mg/L.

experimental values well, and a pseudo-second-order kinetic model, which explained the kinetic data satisfactorily. This pseudo-second-order kinetic model, based more on the adsorption capacity of the adsorbent than on the concentration of the adsorbate in the aqueous solution, is written as follows (Araneda et al., 2008):

$$\frac{dq_t}{dt} = k \cdot (q_e - q_t)^2 \quad (3)$$

In Eq. (3),  $q_e$  and  $q_t$  are the amounts of As(V) ions adsorbed at equilibrium and at time  $t$ , respectively, and both are expressed in mg metal/g adsorbent, while  $k$  denotes the rate constant. The driving force of the process is  $(q_e - q_t)$ , which depends on the number of active and vacant adsorption sites disappearing over time. Integrating Eq. (3) and assuming the boundary conditions  $q_t = 0$  for  $t = 0$  and  $q_t = q_t$  for  $t = t$ , the following expression is obtained:

$$q_t = \frac{q_e^2 \cdot k_2 \cdot t}{1 + q_e \cdot k_2 \cdot t} \quad (4)$$

In Fig. 12, the experimentally observed adsorption kinetic values are compared with those calculated by the pseudo-second-order kinetics model (continuous lines), which have been arranged using Eq. (4). A good agreement between both sets of data was observed. Table 3 shows the parameters calculated by this kinetic model applied to the experimental kinetic values.

The data from Table 3 indicate that an increase in the initial concentration of the metalloid in the aqueous solution resulted in more arsenic being adsorbed at equilibrium, which could be explained by the higher quantity of arsenic available to fill vacant adsorption sites. It is also observed that much higher adsorption rate constants were recorded when a lower initial concentration of As(V) was used in the experiments. This is conclusive, considering that a lower content of arsenic molecules in solution enhances the diffusion rates of the ions in the aqueous film near the surface of the adsorbent. The values of the rate constants determined in this experiments were low, which could be explained by the fact that the adsorption rate decreased strongly after the initial rapid uptake phase; the kinetic model gave an average calculated rate constant for the entire elapsed time. Finally, the measured  $\chi^2$  values confirmed the reasonable low error between the experimental data and the calculated data from the kinetic model, confirming that this pseudo-second-order kinetic model fit the experimental values well. Finally, Table 3 shows that the  $q_e$  values calculated by the kinetic model agree reasonably well with those obtained experimentally.

**Table 3**

Parameters of the pseudo-second-order kinetic model applied to As(V) adsorption on nano-structured calcium silicate modified with Fe(III).

Modified with	As(V) initial concentration [mg/L]	$q_{e \text{ exp.}}$ [mg/g]	$q_{e \text{ calc}}$ [mg/g]	$k$ [g/mg·min]	$\chi^2$ [mg/g]
FeCl <sub>3</sub>	50	6.12	6.10 ± 0.02	0.62 ± 0.031	0.0024
Fe(OH) <sub>3</sub>	50	6.30	6.51 ± 0.11	0.62 ± 0.002	0.0390
FeCl <sub>3</sub>	200	20.29	20.04 ± 0.56	0.02 ± 0.004	1.9604
Fe(OH) <sub>3</sub>	200	23.28	23.82 ± 0.72	0.01 ± 0.001	1.9332

#### 4. Conclusions

The treatment of acidic mine solutions that contain several ionic species was studied by means of an adsorption process using nano-structured calcium silicate hydrate (NanoCSH) modified with Fe(III) as a powerful adsorbent. The synthesis was simple and reproducible using a sodium silicate solution, Ca(OH)<sub>2</sub>, and an iron compound as starting materials. The modification with Fe(III) was carried out by replacing some of the Ca atoms with Fe, utilizing FeCl<sub>3</sub> and Fe(OH)<sub>3</sub> as iron sources. In both cases, an amorphous and stable solid compound was obtained that was slightly more uniform and stable if iron chloride was used in its synthesis. The maximum replacement of Ca atoms by Fe atoms was established to be approximately 13 M%. Compounds created with iron up to this level retained the nano-structure and adsorption capacity close to that of unmodified NanoCSH. Diverse characterization methods confirmed the amorphous character of the adsorbent comprising agglomerates of particles having a mean particle size of 358 nm and an average surface area between 80 and 150 m<sup>2</sup>/g. The compounds had micro and mesopores in the size range between 10 and 20 nm. FTIR and DSC analysis confirmed the presence of free water molecules, silanol groups and O–Si–O bonds.

Chemical analysis indicated contents of 27.95% Ca and 6.18% Fe in the adsorbents. Both adsorbents, based on iron chloride and on iron hydroxide, had similar adsorption capacities, which were nearly unaffected by the initial pH of the waste solutions in the range studied (2.0 to 6.0). Very strong and fast adsorption of these adsorbents was observed towards arsenate, phosphate, Cu(II), Zn(II) and Cd(II) ions. All species were removed almost quantitatively. The adsorption ability depended on the mass of adsorbent employed in the experimental runs and on the initial concentration of the ionic species. Very high maximum capacities close to 55 mg As(V)/g of adsorbent and approximately 80 mg phosphate/g of adsorbent were established in the pH range between 2 and 4. Interestingly, the calcium arsenate and calcium iron arsenate species formed on the surface of the silicate were quite insoluble and potentially allow the safe disposal of spent material in mining tailings. Adsorption extents of 99.94% for Cu(II), 99.98% for Cd(II) and 99.99% for Zn(II) were determined under the same acidity condition, being measured for these metals, concentrations in the raffinate lower than those accepted by the Chilean environmental norm that regulates the discharge of them in natural water bodies.

The hybrid Redlich-Peterson equilibrium isotherm model fit well to the arsenate adsorption experimental results, confirming that the adsorption process is favorable and very intense. It also indicated that the results conformed more closely to the Langmuir than the Freundlich isotherm. Kinetics experiments confirmed a high adsorption rate for all studied ionic species by the synthesized adsorbents in a chemical process governed by a pseudo-second-order kinetic model. This confirmed that the adsorption process strongly depended on the adsorption capacity of the adsorbents.

As a global conclusion, it is possible to state that the modification with Fe(III) of the previously synthesized nano-structured calcium silicate hydrate does not affect its high potential as an adsorbent for treating polluted acidic solutions. If anything, the modified materials were superior to the unmodified material in terms of stability and maintaining their uptake capacity. Both the modified and unmodified silicate acted as seeding material for insoluble hydroxides and salt

species. The presence of iron in the adsorbent structure significantly improved its ability to remove arsenic species by forming highly insoluble and stable double iron and calcium arsenate salts.

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