



Removal of lead and nickel from aqueous solutions by SiO₂ doped potassium titanate

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ABSTRACT

This paper is related to the elimination of Pb²⁺ and Ni²⁺ ions from aqueous solutions by adsorption in potassium tetratitanate doped with silica. The adsorbent was prepared in the form of pellets from potassium polytitanate (45 W%), powdered Pyrex[®] glass (5 W%) and potato starch pastes (50 W%), which were extruded and heat treated at 1100 °C. The physicochemical characteristics of the granulated adsorbent allow the retention of lead from the aqueous solutions when passed through of an adsorption column, and the lead concentration in wastewater can fulfill the maximum permissible limits of national regulations. The experimental techniques used were: ICP, SEM, BET, Mercury Porosimetry and XRD. The nickel ions removal was carried out in sets of systems batches. The effects of the time on flow of the adsorbent and the pH of the solution on the effectiveness of the adsorption of Pb were also investigated. The maximum amounts removed of lead and nickel were 28 and 19.9 mg/g in batch sets. The mechanism of lead and nickel retention on the developed adsorbent is considered as a combination of adsorption, ion-exchange and precipitation processes. At basic pH values and with the adsorption results obtained in this paper proposes a kind of complex surface based on the formation of metal hydroxide on the surface of the original adsorbent. It is also shown that the lead-saturated adsorbent could be stabilized by means of a heat treatment.

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1. Introduction

Industrial activity generates annually tons of heavy metals that contaminate water streams all over the world. Waste of lead is generated from the use of storage batteries, pigments, paints and printing industry as well as petroleum refining industry [1]. The health problems associated with exposition to lead sources, especially for children are well established [2]. Although activated carbon is one of the most effective adsorbents for the removal of lead from wastewater, but its high cost limits the use of this materials for the treatment of lead contaminated industrial effluents [3]. Nickel is a toxic metal, which may be present in wastewaters. Nickel salts are commonly used in metal plating and its concentration in industrial wastewaters range from 3.40 to 900 mg/L. Maximum permissible limit for nickel in bottled water has been fixed as 50 mg/L by European Economic Community [4]. The chronic toxicity of nickel to humans and the environment is well known and high nickel concentration causes lungs and bone cancers. To solve this problem, many efforts has been made to produce an eco-

nomically and technically attractive alternative to substitute the activated carbon as lead and nickel adsorbent [4–7]. Main challenge on this field is to find adsorbent materials that combine cost and efficiency with adequate mechanical properties to be used in adsorption batch and column systems. The mechanical properties of ceramic materials and the possibility to tune their chemical surface properties make possible to develop adsorbent materials with competitive costs based on ceramic compounds. Potassium titanates are ceramic materials which present an important ionic exchange capacity and due to this property, they have been used to remove metals from wastewater like cobalt, nickel and copper according to Cardoso et al. [8] and radioactive elements like Cs¹³⁷, Sr⁹⁰ and U²³⁸ from nuclear wastewater where according to Moon et al. [9], and at pH 2 ionic exchange of K₂Ti₄O₉ shows higher selectivity for Sr²⁺ than that observed for Cs⁺, with distribution coefficients of 3300 and 200 mL/g respectively.

Mishra et al. [10] found in the adsorption of Hg²⁺, Ba²⁺ and Cd²⁺ ions on K₂Ti₆O₁₃ that at pH values of 4.5, the concentration of adsorbed Ba²⁺ under equilibrium was increased from 0.896 × 10^{−8} to 0.813 × 10^{−4} mol/g increasing the Ba(NO₃)₂ concentrations from 10^{−7} to 10^{−3} mol/dm³ and adsorption heat was 11.5 kJ/mol corresponding to the enthalpy of an ionic exchange. The Ba²⁺ adsorption is not affected by the presence of Sr²⁺, Ca²⁺, K⁺ and Cs⁺ ions and an increase has been found for pH values greater of 4.5.

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This kind of studies on the adsorption properties of potassium titanates have been also made for other ions like Hg^{2+} [11], Cd^{2+} [12] and Cu^{2+} [13]. On these studies potassium titanates have been studied mainly as powders, which is not the proper form for industrial applications where as pellets are the mostly used presentation of materials for the packing of adsorption columns.

Recently a new method to obtain ceramic granular adsorbents has been reported by sintering of green bodies prepared by the mixing of semi-crystalline potassium tetratitanate, glass powder (obtained by milling of Pyrex® glass) and potato starch [14]. Tetratitanate ($\text{K}_2\text{Ti}_4\text{O}_9$) doped with SiO_2 has been obtained by chemical interaction of potassium polytitanate ($\text{TiO}_2/\text{K}_2\text{O}=4$) and alumina-borosilicate glass and characterization showed a crystalline structure of high-strength similar to the potassium hexatitanate ($\text{K}_2\text{Ti}_6\text{O}_{13}$).

The synthesized ceramic material presented excellent properties as a well developed porous structure and distribution, surface area ($2.3\text{ m}^2/\text{g}$) and mechanical properties (compressive strength of about 110 MPa). In general, Tetratitanate ($\text{K}_2\text{Ti}_4\text{O}_9$) doped with SiO_2 has demonstrated to have high effectiveness for removal of Pb^{2+} and Ni^{2+} ions from aqueous solutions. In according to the obtained results, $\text{K}_2\text{Ti}_4\text{O}_9$ doped with SiO_2 is a promising material and a alternative as an adsorbent for industrial applications. In this study is reported the mechanism of the interaction of adsorbent with ionic lead and nickel on aqueous solution and an appropriated way for the industrial use of polytitanate based adsorbents. Batches and columns systems have been tested with two different metal ions (Pb^{2+} and Ni^{2+}) to verify the effectiveness of the adsorbents. Batches experiments were carried out to observe the behavior isothermic models and the dynamic systems to observe the good stability of the adsorbent in dynamic flows for long time periods.

2. Experimental

2.1. Adsorbent synthesis

Preparation of adsorbent material was made according to the method of extrusion-heat treatment described by Aguilar et al. [14] Preparation steps are described as follow: semi-crystalline potassium tetratitanate (45 W%), potato starch (50 W%) and milled Pyrex® glass (5 W%) have been mixed until to have a homogeneous mixture and 40% of distilled water was added based on total weight of solids. Cylindrical probes of a diameter of 5 mm and 6 to 9 mm of length were prepared by extrusion of pellets. Samples were dried at 65°C for 1 h and afterwards they were thermally treated at 1100°C for 0.5 h at a heating/cooling rate of $5^\circ\text{C}/\text{min}$. Potassium tetratitanate has been synthesized in according to previous work [15] by means of the thermal treatment of a precursor mixture (10 W% TiO_2 , 8 W% KOH y 82 W% KNO_3) for 1 h at 500°C .

Commercial potato starch was obtained from Sabritas S.A- de C.V., and TiO_2 , KOH and KNO_3 were acquired from Aldrich reagent grade (purity 99%). Nitrogen adsorption was used for the characterization of textural properties in a sorptometer Autosorb1C from Quantachrome.

2.1.1. Porosity and specific surface area in the granular adsorbent

By mercury porosimetry analysis was found that synthesized adsorbent based on Potassium Titanates had a 35% of porosity, mean size of transport pore of 0.4 microns, macropores in a range from 0.05 to 0.4 microns of diameter and mesopores with diameters less than 0.05 microns, in a intricated structure.

The specific surface area of the solid ($\text{K}_2\text{Ti}_6\text{O}_{13}$ doped with SiO_2) was determined by the BET methodology and it was found to be $0.65\text{ m}^2/\text{g}$ before the removal process.

Three sections in the column have been measured after the removal process and the results were in the bottom = 1.65, middle = 1.82 and the top $2.82\text{ m}^2/\text{g}$. In Fig. 1 is shown a summary of these measurements.

2.1.2. Calculation and prediction of phases

FactSage software has been used to calculate phases could precipitate and phase transformation during adsorption processes in the aqueous systems.

2.2. Chemical reagents and solutions (columns)

Lead Nitrate (Aldrich, 99% of purity) was used for adsorption tests in aqueous solution at a concentration of 155 mg/L in distilled water and a pH of 5.6. This solution (No. 1) was used on direct adsorption tests. In addition, solution 2 was prepared by mixing of nitric acid (1 M) and solution No. 1 to adjust pH to 3.5. Both solutions have been used to study the effect of pH on the efficiency and mechanism of Pb^{2+} removal from acid solutions, which is the most common condition found in industrial waste water [16]. In previous works only the authors investigated in batches systems. The amount selected for 155 mg/L is approximated than that more effective in batches.

All experiments were made at $23 \pm 2^\circ\text{C}$. A glass column (adsorber) of 25 mm of diameter and volume of 75 cm^3 was used and filled with 165 g of adsorbent pellets, and the packing volume obtained was 70 cm^3 . The aqueous solution was poured into to the column using a system of two attached vessels located over the column with a stable hydrostatic pressure of liquid (Fig. 1).

At starting, flow rate was made at $2 V_0/H$ ($140\text{ cm}^3/\text{H}$), which is a typical value for the operation of industrial adsorption columns [17]. To determine the flow rate, solution passing through packing was collected in a vessel and to study the lead retention mechanism, pH and evaluation of K and Pb concentrations. ICP Spectrometry of Iris Intrepid II by Thermoelemental Thermojarrel Ash, was used in the elemental analysis.

2.3. Ni batch solutions preparation

All experiments were carried out in sets. Solutions with 100 and 200 mg/L of Ni^{2+} were prepared using $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (Aldrich, company) and these solutions were used for Ni(II) ion stock during the adsorption experiments. All acids and bases were purchased from Merck and they were analytical grade. Distilled water by Milli-Q System (Millipore, USA) was used during the experimental studies. The pH meter was calibrated with pH buffer solutions by Merck of values 4, 7 and 10.

2.4. Adsorption of Ni and kinetic properties of Ni adsorption

Experiments in batches of Nickel were carried out using a series of Erlenmeyer flasks of 200 mL of capacity covered with Teflon sheets to prevent any foreign particle contamination. Effects of pH, concentration, dose, and shaking time were studied in this stage.

Isotherms have been run by taking different concentrations of Ni at the desired temperature and pH. These concentrations were decided after a good deal of preliminary investigation. After, the solutions were centrifuged and Nickel concentrations were determined in a supernatant using an Atomic Absorption Spectrometer.

Batch technique has been used due to its simplicity to determine the kinetic. A series of Erlenmeyer flasks of capacity 200 mL containing a definite volume of solutions of nickel of known concentrations were kept in a thermostatic shaking water bath. After the desired temperature was attained, a known amount of the adsorbent was added to each flask and the flasks were agitated mechanically. At given time intervals (from 0 to 1 h, samples were

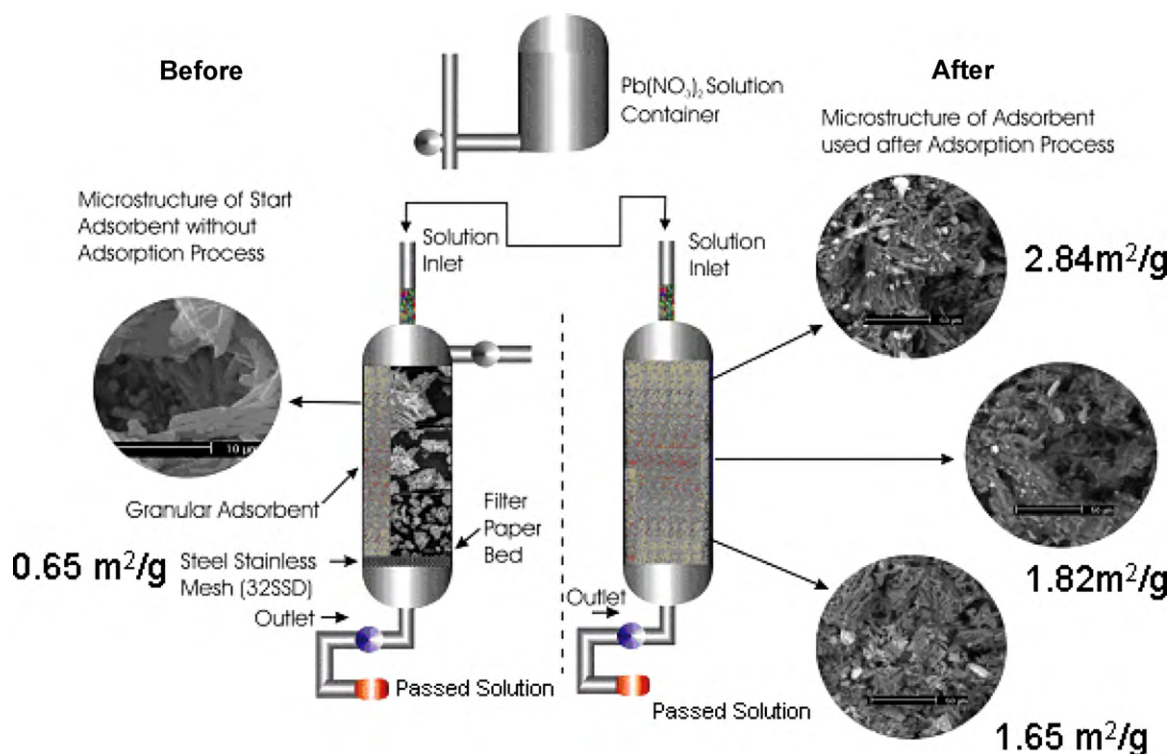


Fig. 1. Experimental arrangement for dynamic column studies.

collected each 15 m, after that, each hour until to complete 7 h), the solutions were centrifuged and the supernatants were analyzed for nickel using the Atomic Absorption Spectrometer. Equilibrium was achieved in 60 min for nickel.

The removal for nickel was developed by the Langmuir adsorption equation:

$$1/Q_{eq} = 1/Q_0 + 1/bQ_0 + 1/C_{eq} \quad (1)$$

where Q_{eq} is equilibrium metal ion uptake (mg/g), C_{eq} the equilibrium concentration in solution (mg/L), Q_0 represents the maximum uptake of metal ion (mg/g) and b is a constant related to the energy of adsorption (L/mg).

2.5. Characterization of adsorbents after adsorption tests

Saturated adsorbents after runs were dried at 95 °C during 2 h and analyzed in a X-ray Diffractometer by Philips X'Pert using $K_{\alpha}(Cu)$ radiation, a secondary monochromator (Ni filtering) at 40 kV and 30 mA.

SEM analysis were made in a Scanning Electron Microscope Philips XL30, ESEM (Environmental Scanning Electron Microscope) equipped with EDS (Pegasus, operated at 20 kV of acceleration voltage).

The dried adsorbent was milled and screened in a standard sieve mesh 10 and tablets of 10 mm of diameter and 15 mm of height were prepared by compression with a load of 192 MPa and thermally treated at 1100 °C during 1 h to sinter the ceramic material.

Several tests have been applied to the sintered tablets. Strength Compression and Leachability tests have been made in according to the ASTM C773-88 and GOST 1694-84 standards, respectively. In Leachability tests a sample of 10 g of ceramic material have been dissolved in 100 ml of distilled water at 96 °C during 5 h and analyzed by ICP to determine the lead ion content according to the procedure established in reference [18].

3. Results and discussion

3.1. Adsorption tests in column and effect of pH and reaction time.

In Table 1 is shown the amount of lead retained after adsorption experiments for aqueous solutions at the two pH levels of this study. As can be seen lead was removed from solution and in the case of the solution at pH 5.6 the amount of PbO is longer than 10% (w/w). For treatment under this condition the content of lead in solution changed from 155 to 0.05 to 0.1 ppm. The remained content of lead is within the specified for industrial wastewater discharge [18].

For contact time of 3 h or higher the changes on lead concentration for the aqueous solution were minimal.

For solution at pH 3.5, the lower lead content for treated solution was of 14–23 ppm. In Fig. 2 is shown an increase in the potassium content by the pass of solution in adsorption treatment of Pb^{2+} . Potassium concentration in solution was higher in a pH value of 3.5

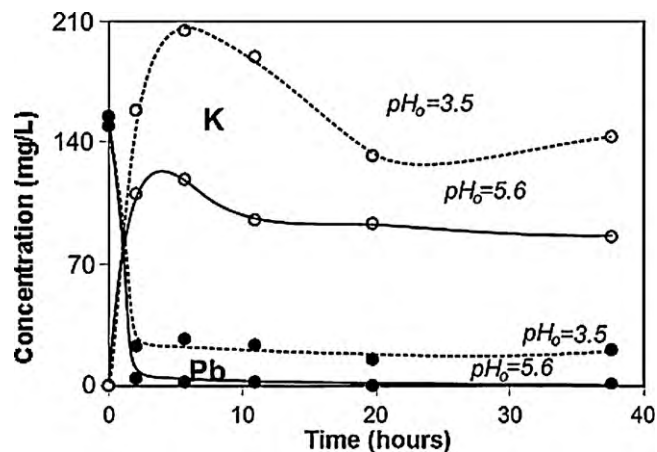


Fig. 2. Effect of contact time on the content of Pb and K in the passed aqueous solution prepared at pH of 3.5 and 5.6.

Table 1
Chemical analysis (columns) of potassium titanate before and after adsorption treatment. Results obtained from eight analyses taken from different parts of sample.

Adsorbent	Metal oxide (wt.%)			
	SiO ₂	K ₂ O	TiO ₂	PbO
Before adsorption treatment	9.8 ± 2.2	15.5 ± 3.2	73.8 ± 1.9	0
After adsorption treatment under pH ₀ 5.6	3.8 ± 0.9	13.0 ± 2.2	64.5 ± 7.9	10.8 ± 4.6
After adsorption treatment under pH ₀ 3.5	3.5 ± 0.7	12.8 ± 1.3	64.1 ± 5.0	9.9 ± 5.9

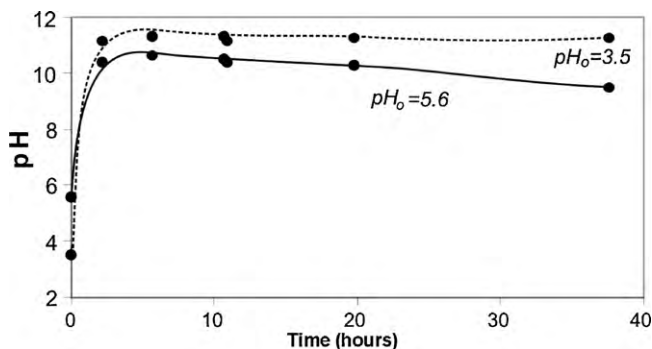


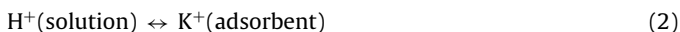
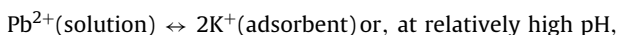
Fig. 3. Effect of contact time on the evolution of pH of passed aqueous solution.

than 5.6 and in both cases a maximum concentration was reached in times less than 5 h. In addition, stabilization in the potassium concentration was reached below the maximum concentration. The supply of the metal solution was continuous during the total time for each experiment.

The adsorption process involves the following [19]:



Taking into account high ion-exchange properties of different potassium titanates [10], the interaction between Pb (contained in aqueous solution) and the applied potassium titanate could involve two parallel ion-exchange processes [20,23]:



The higher concentration of protons for a pH value of 3.5 promotes the exchange between H⁺ and K⁺ ions, thus higher content of lead ions remain in solution. The exchange of potassium ions of the adsorbent by protons on solution increased the pH values of 3.5 to 11.3, and 5.6 to 10.6 in solution. Fig. 3 shows the influence of time and original pH value on the pH of solution after treatment of removal.

Obtained results confirm that adsorbent based in potassium tetratitanate doped with SiO₂ promotes the removal of lead from aqueous solutions. A better performance of adsorbent was found when the slightly acid solution (pH 5.6) was used. The pH in the aqueous solution of Lead, affected the ratio of chemical species [15]. Pb²⁺ ions are predominant at pH values below of 5. However besides Pb²⁺, a high content of Pb(OH)⁺ can also be found at pH values between 5 and 6. The precipitation of Pb(OH)₂ is favored at pH values up to 6.

In according to Zheng et al. [21] and Nunes et al. [22] potassium titanate has a high hydration rate and is transformed to the hydrated state, increasing thus the pH value and the content of K⁺ in the aqueous solution. At the starting of adsorbent/solution interaction, two parallel processes are present, the adsorption of Pb²⁺ and/or PbOH⁺ ions on the potassium titanate surface, and the

hydrolysis of this adsorbent. After the adsorption of Pb²⁺ ions, these ions take part in the ion exchange process with K⁺ cations located at channels of the adsorbent (Fig. 10) and the increase of pH promotes the precipitation of Pb(OH)₂ on adsorbent surface.

Also the adsorption processes have a high dependency of the pH.

The effect of the influence of pH on the adsorption processes can be explained with the help of loading effects on the adsorbent surface as follows.

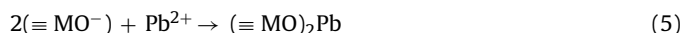
The speciation of Pb²⁺ depends of pH, [30]. While in a pH range from 2 to 5 lead there exist always and exclusively as Pb²⁺, to a value greater than 8 this is hydrolyzed to PbOH⁺ and Pb(OH)₂ (eqs. (1)–(2)).



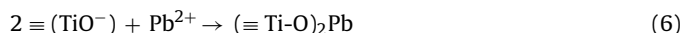
At a pH of 2, the kind that prevails is the Pb²⁺. Similarly, due to reaction (eq. (3)) the adsorbed surface is positively charged. As the two possible charges, they repel each other adsorption efficiency decreases (when M = Metal).



A higher pH the adsorbent surface becomes negatively charged due to dissociation (equation 4) and which can be adsorbed Pb²⁺ and Pb(OH)⁺. (eq. (5)).

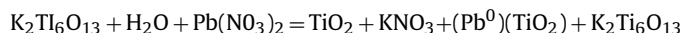


For the adsorbent, the affinity of Pb²⁺ to the surface can be described by eq. (6).



In this work preliminary tests were evaluated to observe the interaction between water and the adsorbent without the application of metal solutions. As result of this pH value after of 24 h was 10.6. With this consideration can be explained the formation of a small quantity of hydroxocarbonates or the possibility of the presence of surface complex as Hydrocerussite (Pb₃(CO₃)₂(OH)₂) than it can occurs at pH values from 4 to 5.

Calculate phases in adsorption lead and potassium titanates in aqueous systems can be as follow:



This calculate based of 1 mol for each compound.

Column test were made under constant hydraulic pressure. Fig. 4 shows the decrease of solution flow rate as a function of time on flow. As can be seen, flow remained constant almost during 10 h for solution with the higher pH, afterwards a trend of flow decrease is observed. For more acid solution the flow reduction trend was evident below 5 h.

3.2. Ni adsorption batch and pH studies of Nickel ions removal

Adsorption of Ni(II) on to adsorbent was systematically investigated by parameters such as initial concentration of Ni(II) ion in

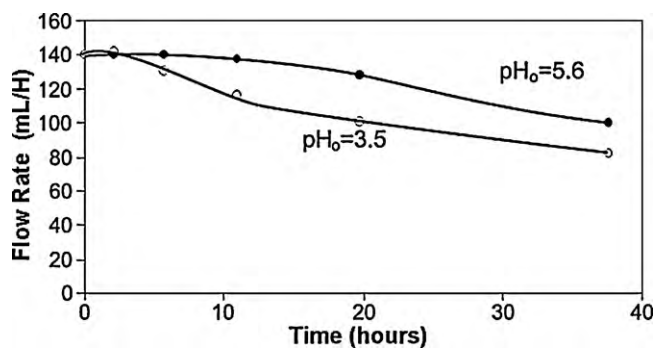


Fig. 4. Effect of contact time on the flow rate of aqueous solution.

solution, contact time, pH where single solution of Ni(II) ion was used. Maximum amount removed for nickel ions was 19.9 mg/g of adsorbent. At 7.5 pH value and 99.94% of total effectiveness of removal. This results are similar with those obtained by [26] and [29].

Fig. 6 shows nickel adsorption isotherms on contact time from experiments with 200 mg/L of Ni^{2+} with 7.5 and 8.0 starting pH values. The concentration of Ni^{2+} in the aqueous phase also changes from the initial added Ni^{2+} concentration to zero over a narrow pH range. The pH range over which Ni^{2+} is removed by adsorption in this study is 7.0–8.0 which is similar to that found by [27] for Ni^{2+} adsorption on hydrated oxides of Iron and Chromium. Fig. 7 shows removal percent of Ni^{2+} developed with start pH value of 7.0.

For the metal ion adsorbate, the percentage removal of the metal nickel is enhanced by the presence of an adsorbing surface at any given pH. The pH range over which adsorption (for example) takes place will depend to some extent on factors such as surface area and metal ion concentration. The extent of removal, at any given pH, resulting from coprecipitation is greater than the extent of removal resulting from adsorption for Ni^{2+} .

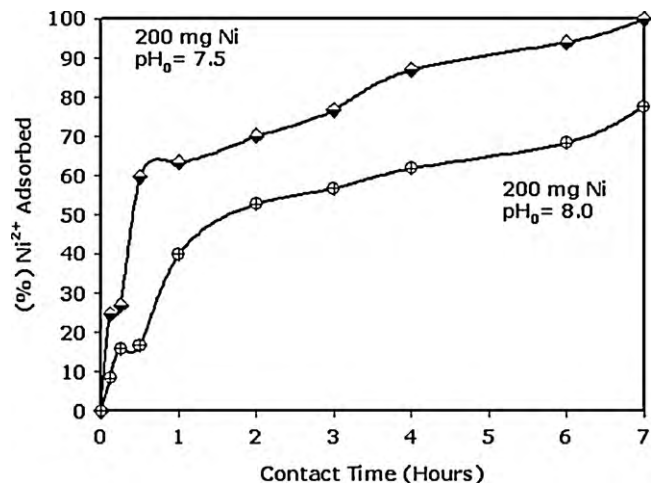
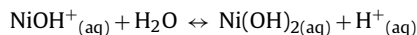
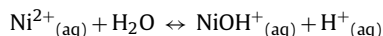
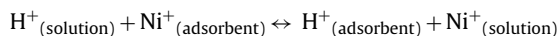


Fig. 6. Effect of Contact time on Ni^{2+} ions removal percentage in silica doped potassium titanates adsorbents. Batch results.

The main reactions for nickel ions can be presented as follows:



And the ion exchange of nickel adsorption could be as follows:



The following reaction of hydrolysis and adsorption can be presented in the solid solution interface.

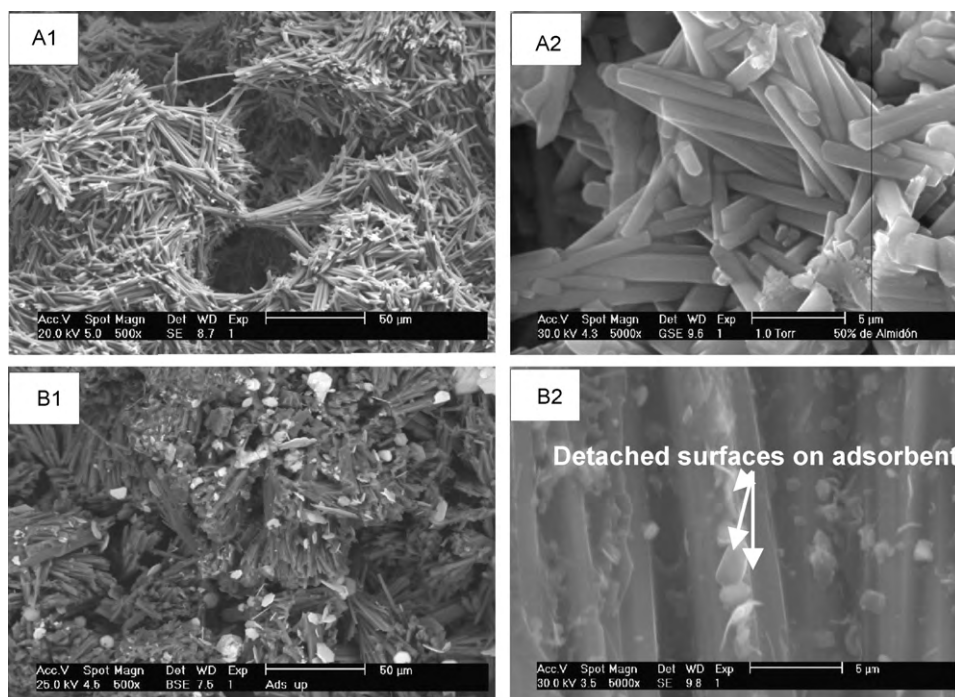
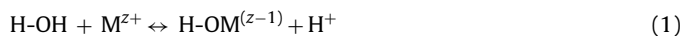


Fig. 5. SEM images of potassium titanate (A) before and (B) after adsorption treatment at 100 h of contact time. Magnification 500× (1) and 5000× (2).

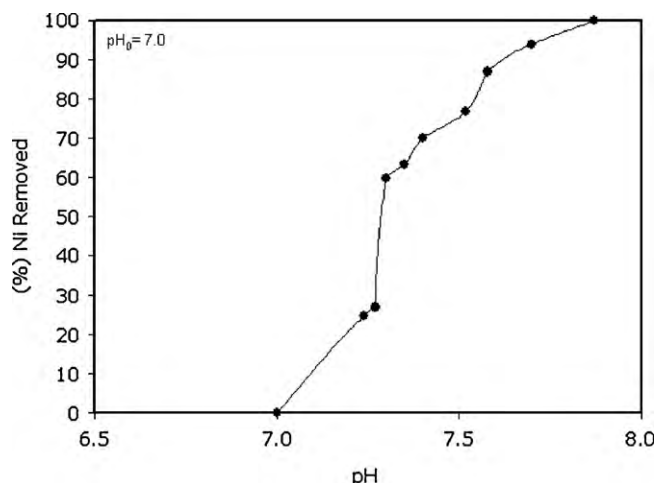


Fig. 7. Effect on start pH Ni^{2+} in the removal of Ni^{2+} ions on adsorption in silica doped potassium titanates adsorbents. Batch results.

From the experimental data is clear that the Ni^{2+} removal increase slowly and gets a maximum in a longer period of time. The consumption of nickel is faster on the start stages, and at the final stages can be constant.

The metal ions compete with the protons to obtain the surface sites.



3.3. SEM analysis

SEM analysis revealed that, during the contact between solution and adsorbent for the removal of lead, morphology of potassium

titanate particles changed (exfoliation and intercalation)[28] and particle size was increased twice as it can be observed in Fig. 5.

Textural characterization of used adsorbent indicated that the surface area was increased 30% of its original value. By SEM analysis was found that some particles segregated from matrix presented a chemical composition rich in Lead (47.8 ± 3.1 wt % PbO) and the ratio $\text{K}_2\text{O}/\text{TiO}_2$ was similar to potassium tetratitanate rather than the ratio of potassium hexatitanate. Theoretically, the maximum PbO content (for a total replacement of potassium) corresponds to 32% W of the exchanged titanate, thus, apparently the deposition of lead on these particles was not only by ionic exchange but also by Lead precipitation. The calculation was made taking into account that the limit is in agreement with the initial composition (% weight): $\text{SiO}_2 = 9.8$, $\text{K}_2\text{O} = 15.5$, $\text{TiO}_2 = 73.8$, and which corresponds to the composition as (% molar): $\text{SiO}_2 = 13.0$, $\text{K}_2\text{O} = 13.5$ and $\text{TiO}_2 = 73.5$. Thus if the entire K_2O content is replaced with the entire content of PbO gives the result of a change in W%, and which is given in Table 2.

The matrix of potassium titanate showed a composition with $78.1 \pm 2.2\%$ of TiO_2 , $17.7 \pm 2.1\%$ of K_2O , $3.5 \pm 0.5\%$ of SiO_2 and $1.8 \pm 0.3\%$ of PbO, which represent only the exchange of around 4% mole of the K_2O available. General chemical composition before and after of the purification for adsorption with pH solution of 5.6 is shown in Table 1, and for this case, the Lead quantified on titanate corresponds to an exchange of around 26% of all the K_2O available at the beginning of the treatment.

The adsorbent used during 40 h and subsequently heat treated at 1100°C showed a crystalline structure formed by acicular needles like the untreated sample, and the sintering process become evident as can be seen in Figs. 5 and 9.

Fig. 8, shows two SEM photomicrographs of adsorbents coated by nickel particles, chemical composition by EDS inside of fibers was: W% = 73.3TiO₂, 18.5K₂O and 8.2SiO₂. Chemical composi-

Table 2
TiO₂/K₂O relationships for pure titanates and using SiO₂ in metallic removal columns treatment.

Comp.	SiO ₂	K ₂ O	TiO ₂	Total
W% (EDS) A	9.8 ± 2.2	15.5 ± 3.2	73.8 ± 1.9	100.0
Mol. weight *B	60.08	94.19	79.89	
Mole fraction (A/*B)* = g mol ⁻¹	0.163	0.165	0.924	1.252
Mol%				
M% (EDS)	13.03	13.17	73.80	100
R = (TiO ₂ /K ₂ O)				
Theoretical K ₂ Ti ₆ O ₁₃ = (TiO ₂ /K ₂ O) = 5.60			Real = (TiO ₂ + SiO ₂)/K ₂ O = 6.414	
W% If it is changed all content of K ₂ O by PbO				
SiO ₂ (g mol ⁻¹)	PbO (g mol ⁻¹)	TiO ₂ (g mol ⁻¹)	Total	
60.08 × 13.03 = 782.24	223.2 (PbO) × 13.17 = 2939.54	79.89 × 73.8 = 5895.8	9617.58	
8.13%	30.56%	61.31%	100%	

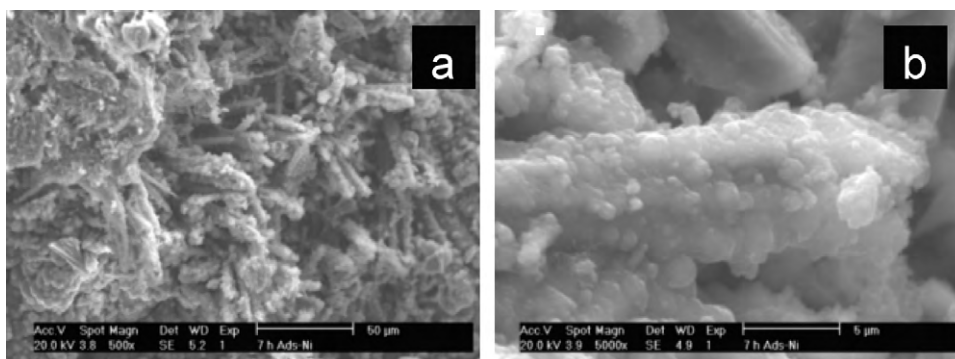


Fig. 8. SEM images, (a) adsorbent with nickel fine particles above its surface (500×), (b) Same material 5000×. Both of them was taken in high vacuum mode with secondary electrons.

tion above fibers was: W%=50.6NiO, 32.8, TiO₂ 11.5K₂O and 5.1SiO₂.

3.4. XRD analysis

Fig. 9 shows the XRD patterns of samples before and after of the adsorption treatment, it is possible to observe that potassium tetratitanate doped with SiO₂ (K₂Ti₆O₁₃ = chart # 74-0275 ICDD database) structure is preserved and only small signals corresponding to PbO (Lead Titanium Oxide chart # 06-0452, ICDD data base) are formed due to the oxidation of Pb²⁺ during the the heat treatment. The XRD pattern for nickel titanate was identified with chart # 01-76-0334.

PbO content on samples of potassium titanate after adsorption (10.8±4.6%) and after adsorption and sintering treatment (10.9±3.2%) indicates that lead is not lost during thermal treatment, since the values are within the experimental error of measurement. In According to the last, there is no risk in the sintering of exhausted adsorbents once saturation with Pb is reached.

3.5. Mechanical properties of heat treated samples

Compressive strength tests in sintered samples showed results of 280±22 and 345±12 MPa for samples with Lead and Nickel, respectively. Leachability resistance test was made by immersion in water at 96 °C during 6 h. Lead in water was lower than 0.002% and the nickel was lower than 0.006%, which indicates that both oxides have been stabilized on the titanate substrates, the risk of contamination by lixiviation is negligible after adsorbent disposal (Fig. 10).

The contact of the adsorbent with the aqueous solution of Pb promotes the degradation of surface as a consequence of saturation, transformation of the structure and change of the crystal morphology. These processes are produced by the hydrolysis of the SiO₂-doped potassium titanate, which is faster due to the transformation of tetrahedral silica that substitutes octahedral titania in potassium silicates that are soluble in water [24]. This SiO₂ dissolution promotes the degradation of adsorbent structure and increasing the size of pore channels [24]. This process explains the lost of SiO₂ on adsorbent which changes from 9.8 to 3.8 wt% as is shown in Table 1, as well as the increase of diameter of potas-

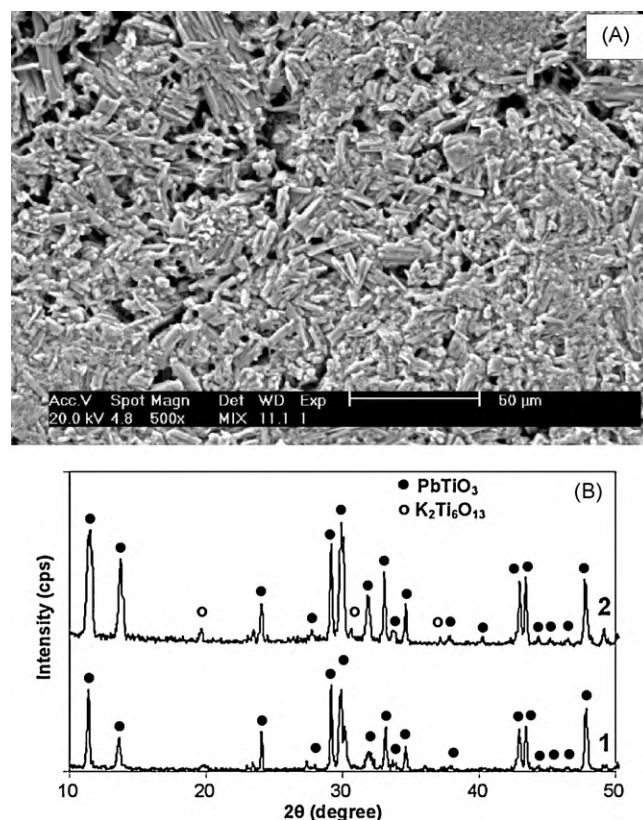


Fig. 9. SEM image of spent adsorbent after 38 h of contact time and thermal treatment and (A) XRD spectra (of this adsorbent) (B) before (1) and after (2) the thermal treatment made at 1100 °C. Main signals correspond to K₂Ti₆O₁₃ and PbTiO₃ (○).

sium titanate fibers (Fig. 5). In According to the SEM study, the surface of potassium titanate fibers is saturated with Pb²⁺ and gradually, flakes are formed and detached from surface (Fig. 5b2). The exfoliated flakes of Pb(OH)₂ and potassium silicates dissolved are deposited in pores (Fig. 5b1 and b2) which is confirmed by EDS analysis where TiO₂, K₂O, SiO₂ and a high content of PbO have been

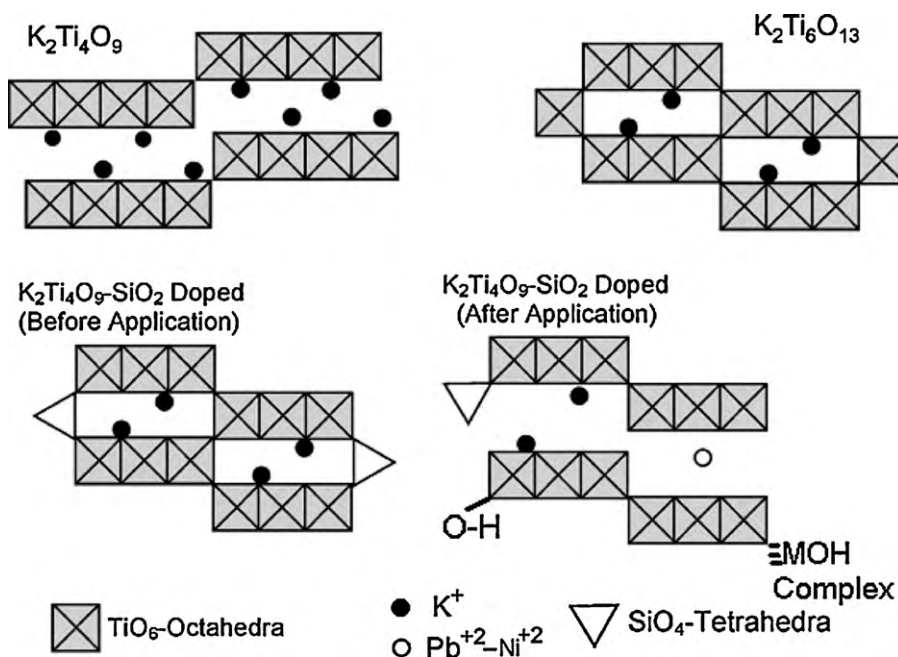


Fig. 10. Structural model of titanates and representation of SiO₂ doping and lead ion exchange.

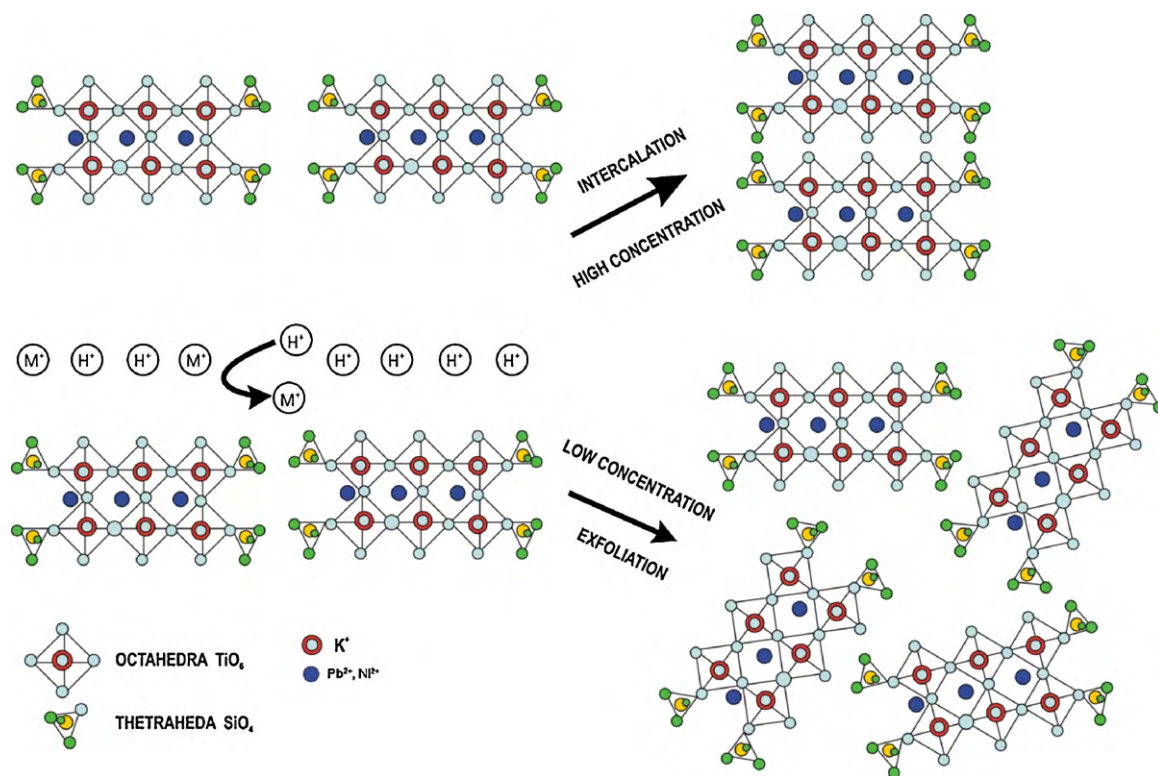


Fig. 11. Exfoliation and intercalation diagrams for titanates in metallic adsorption processes.

determined. These changes on the structure promote the degradation of the porous system on the adsorbent and even an increase in surface area is detected as a consequence of the opening of some channels in the fibers. The effectiveness of lead removal is diminished due to the reduction of flow rate through the adsorbent. (Fig. 5, B1 in comparison with Fig. 5 A1). In Fig. 11 is showed the two probable mechanism of reaction of metal ion at adsorption processes with potassium titanates.

For slightly acid solutions such as pH values between 5 and 6 the stability of adsorbent is higher, for a time period of 40 h. For solutions with a pH value of 3.6 the hydrolysis rate and the structural degradation rate are faster, thus reducing the lead removal rate (Fig. 3) and the effectiveness of lead removal for treatments of 2 h (Fig. 2). The re-use of exhausted adsorbents after regeneration treatments with acidic solutions is well known [7,16,25]. However the confining of the saturated solutions of lead obtained during the regeneration treatment represents a complicated problem. For potassium titanate adsorbent the structural degradation generated during the adsorption treatment limit the efficiency of acid regeneration. In spite of this disadvantage there are some benefits like its safety disposal after thermal treatment since the lead is stabilized in the structure as PbTiO₃, which is a very stable chemical compound. The heat treated spent adsorbent also can be used in some practical applications without environmental risks, as manufacturing of ceramic substrates for the electric heaters (Pb) and pigments (Ni).

Potassium Titanates compounds exhibit properties and behavior unique than the rest of the others oxides (with structure as MO, MO₂ or M₂O₃, etc.). Current studies reporting the characteristics interface-the adsorbed layer and the matrix of the adsorbent even are not studied.

4. Conclusions

The ceramic adsorbent based in a potassium titanate doped with silica (granulated form) was supported in an adsorption col-

umn and final results have shown the capacity for removal of lead and nickel from aqueous solutions. The mechanism for removal of metallic ions consist of an adsorption process combined with ionic exchange and precipitation. During the continuous contact time the structural integrity of pellets is affected, changing the aqueous flow rate. After reaching the maximum adsorption capacity the adsorbent can be heat treated to stabilize lead or nickel in the structure of the ceramic as PbTiO₃ or NiTiO₃. The inert condition of the obtained ceramic allows its use for several applications such as ceramic substrates and pigments.

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