# ZEOTREAT: MULTIFUNCTIONAL ADSORBENTS FOR METAL AND SULPHATE REMOVAL IN MINING WASTEWATERS FROM COPPER INDUSTRY, CHILEAN CASE

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## ABSTRACT

Over the last 5 years Fundación Chile's Environment Program has carried out specific research for the development, adaptation and implementation of innovative technologies for the treatment of mining wastewaters with metal and sulphate content, incorporating the concept of waste recovery and water reuse. One of the most well developed technologies is ZEOTREAT™ which involves the chemical modification of Chilean natural zeolites to obtain multi-adsorbent material for the removal of specific contaminants.

The modified zeolites are an organo-mineral complex obtained from the treatment of mordenite (a type of zeolite from Chile) with a cationic detergent. They have the ability to adsorb oxyanions of: arsenic, As(III) and As(V), molybdenum, selenium and sulfur (sulphate), without losing the natural capacity to adsorb cations such as: copper, nickel, lead, among other.

This technology provides an integral solution for the treatment of mining wastewaters and also has advantages in diluted matrices where there are no conventional, cost-efficient alternatives. The wastewater treatment system is based on a continuous flow where the contaminants are adsorbed in packed columns which contain the adsorbent; either upgraded and/or modified zeolites, depending on the specific application needed.

## 1. INTRODUCTION

Chile is the world's biggest copper producer. This means that aside from all the benefits, large quantities of wastewaters with different physical-chemical characteristics are produced during the extraction and concentration process. Accordingly, these wastewaters need different treatment technologies.

Different studies have shown the ability of activated and modified zeolites (SMZ) to remove cations and oxyanions, respectively [1,2]. A Chilean mining company that commercializes natural zeolites expressed an interest in evaluating the use of zeolites for wastewater treatment in order to maximize the use of this material. Since these kinds of sorbents are relatively inexpensive, SMZ would be a competitive alternative compared to conventional technologies like activated carbon adsorption, ion exchange and synthetics resins.

Zeolites are hydrated aluminosilicates consisting of three-dimensional networks of $SiO_4$ and $AlO_4$, linked by their oxygen atoms. These minerals have a negative charge compensated by the presence of exchangeable- native cations such as calcium, sodium, magnesium, potassium, among others [3]. These structures provide the material with multiple properties that make them useful for industrial applications where they can be modified for adsorption, ion exchange and catalytic processes [4].

The scope of this work was to modify zeolites by the addition of a cationic detergent, ODA (octadecylammonium acetate), in order to use them for exchanging oxyanions like arsenite, arsenate, sulphate and molybdate present in mining wastewaters. The results obtained from the removal of heavy metals by using activated zeolites are also shown in this review. The study also included feasibility studies at laboratory and pilot scale in order to validate the developed technology for the treatment of mining wastewater.

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## 2. EXPERIMENTAL METHOD

Natural zeolites, with the test formula ($Na_{0.6}$, $K_{0.088}$, $Ca_1$) [($Al_2Si_8O_{12}$)] * $7H_2O$ [5] were obtained from mineral deposits located in Chile's central zone. Two different sizes of zeolites were used, 3.35 – 4.75 mm and 0.6 – 1 mm. The modification of Chilean zeolites was carried out in a two step process: First, the zeolite was activated by shaking in aqueous solution of HCl 1 M at 20 °C, for 4 hours using a solid: liquid ratio of 1:2. In the second step, the activated zeolite was treated with an aqueous solution of ODA 0.2 M, dissolved in 5 % acetic acid. The reaction was carried out at 60°C for 24 hours. Other modifications of activated zeolites were also performed by adding surfactants HDTMA (hexadecyltrimetilammonium bromide)[6] and Oleyamine[7] in both cases with concentrations of 0.15 M at 25°C for 24 hours. Both batch and continuous systems were used for the activation and modification of the zeolite and ion exchange experiments.

Synthetic solutions of sodium arsenite, $NaAsO_2$, Arsenic standard (As(V)), sodium sulphate and sodium molybdate were prepared for the laboratory scale studies. All chemicals used were analytical grade reagents and high-purity deionizer water.

Adsorption isotherms of anions in modified zeolites were obtained using batch equilibration techniques. The synthetic stock solutions were mixed with the zeolites using a magnetic stirrer at 25°C, and filtered after a 24 h contact time. The concentrations of the ions in the supernatants were measured. Appropriate solutions and blanks were included in each batch test.

For the kinetic studies, batch tests were used putting the synthetic stock solutions into contact with the zeolites using a magnetic stirrer. Samples were taken at different times.

For feasibility studies wastewater samples from different mining processes were used. The tests were conducted in continuous flow by using embedded columns with zeolites. Each treatment configuration was designed depending on the kind of wastewater treated. For the efficiency analysis the removal rates of ions were measured.

A pilot study was performed replicating the operational conditions used in the laboratory. The pilot was performed at the installations of a copper mining company in order to validate the technology. The pilot plant study used two columns embedded with zeolites, the first with activated zeolites for copper removal and the second with modified zeolites for molybdate removal. Each column contained 250 Kg of adsorbent material.

## 3. RESULTS AND DISCUSSION

The results are shown in the order in which they were developed, considering four stages over a period of four years:

1. Initial Research. Development of different modified zeolites for removal of arsenic, molybdenum and sulphate
2. Applied Research. Pollutant removal studies
3. Application of ZEOTREAT technology. Technical feasibility studies in different mining wastewaters
4. Scale-up of ZEOTREAT technology

Stages 1, 2 and 3 were carried out at laboratory scale. The fourth stage was conducted at pilot scale.

### Stage 1: Modification Process and Capacity of Modified Zeolites to Adsorb Oxyanions:

A family of activated-modified zeolites was obtained at laboratory scale. The effectiveness of the modification process was evaluated through the adsorption capacity obtained from the different types of modified zeolites. All the tests at this stage were conducted in batch systems using the synthetic solutions to analyze the removal capacity of the modified zeolites.

Different studies show that the capacity of the modified zeolites to adsorb oxyanions depends on the type of cationic surfactant used for the modification and on the size of the natural zeolite used[8]. In order to compare the different surfactants used for the zeolite modification (HDTMA, ODA and Oleyamine), batch tests were conducted. The results are shown in Figure 1.

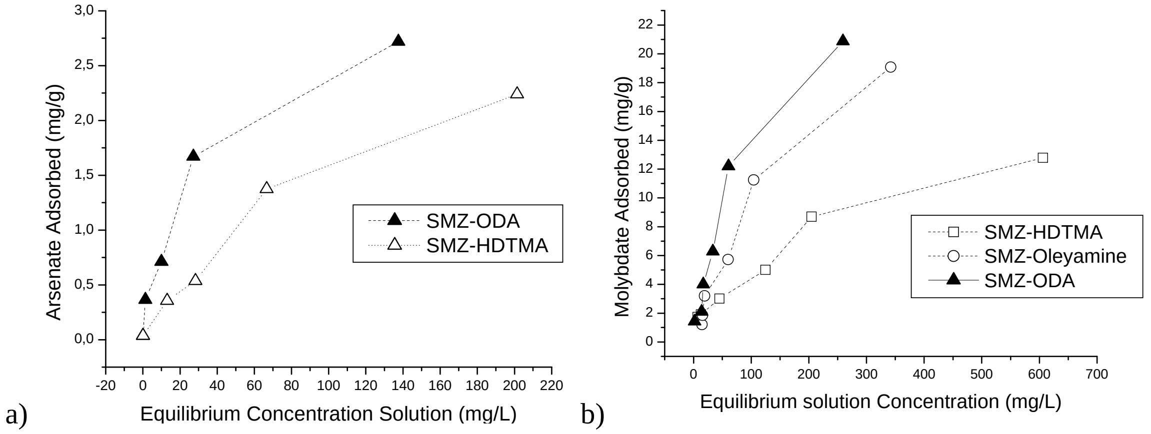



Figure 1. Oxyanion adsorbing capacity of different surfactant modified zeolites. Figure 1a) and 1b), Arsenate and molybdate adsorbing capacity, respectively.

In order to evaluate the performance of the different modification processes, the oxyanion adsorption capacity is the most important factor. The results obtained for arsenate and molybdate adsorption clearly show that the modified zeolites using ODA exhibit higher adsorption capacity compared to the zeolites modified with HDTMA and Oleyamine. The maximum adsorption capacity came to 2.8 mg/g for arsenate and 20.8 mg/g for molybdate when the initial concentration was 1000 mg/L.

The results obtained for sulphate removal are slightly different from previous trends. Results are shown in Figure 2.

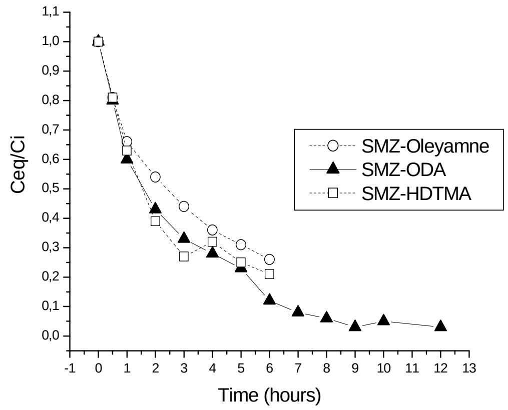
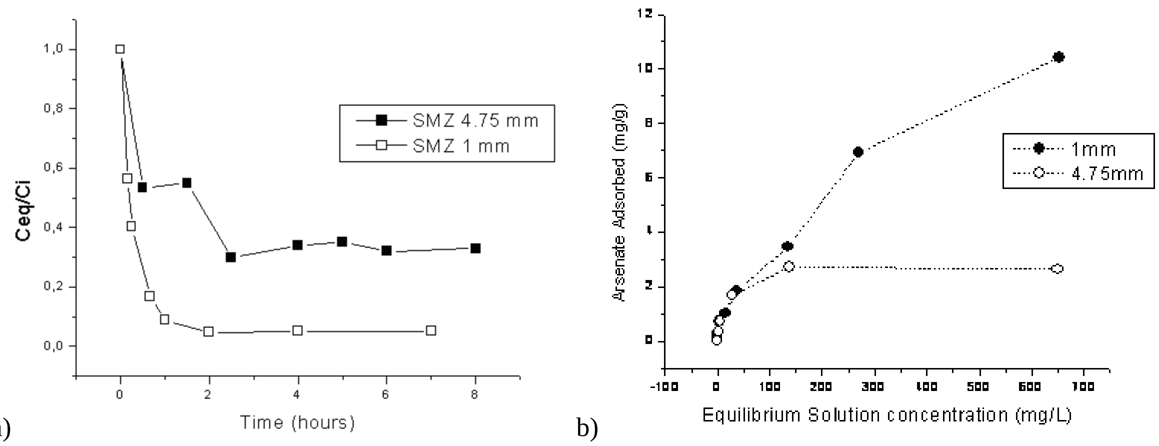



Figure 2. Sulphate adsorbing capacity of different surfactant modified zeolites. y- axis shows the relation between the equilibrium concentration and initial concentration. Initial sulphate concentration: 1000 mg/L, solid- liquid ratio 1:30

The sulphate removal from the solution as a function of the contact time can be seen. Sulphate adsorption behavior was similar for the different modified zeolites, SMZ-ODA, SMZ-Oleyamine and SMZ-HDTMA. After 6 hours of contact time 80 % of the sulphate was removed from the solution.

According to the results obtained in Figure 1 and 2, ODA was selected as the best cationic surfactant for modifying zeolites in order to achieve the removal of all oxyanions considered in this research.

As mentioned above different studies have shown the effect of the size of natural zeolites on the adsorption capacity of contaminants as well as on the time needed to reach the equilibrium between the adsorption sites and the contaminating molecules[9]. The experimental results are shown in Figure 3.




a) b)

Figure 3. Size effect of SMZ-ODA on arsenate removal. Figures 3a) and 3b) show the kinetics and isotherms of arsenate adsorption for both sizes, respectively. Two different sizes were tested, 1 and 4.75 mm.

The results obtained show that the size of the natural zeolite had two important effects on the arsenate adsorption. First, the time needed to reach the equilibrium decreased by 50 % (see figure 3b) and second, the adsorption capacity increased reaching a maximum of 10.3 mg of As/g SMZ when the cationic surfactant used was ODA and the zeolite size was 1 mm (see Figure 1b).

In order to understand the oxyanion adsorption mechanism in the zeolites, an experiment was conducted using synthetic solutions of arsenate and arsenite as oxyanions and natural activated- and modified zeolites as adsorbent materials. The initial concentration of arsenic was 100 mg/L. The experimental results of the oxyanion removal are shown in Table 1 and expressed in removal percentages.

Table 1. Removal expressed in percentage of inorganic forms of arsenic, using different kinds of zeolites

| Adsorbents | Arsenite | Arsenate |
|---|---|---|
| Natural Zeolites | 5 | 16 |
| Activated Zeolites | 15 | 50 |
| Modified Zeolites | 70 | 90 |

According to the results the modified zeolites have a higher capacity for adsorbing arsenic when compared with natural and activated zeolites. The requirement of using modified or pre-treated natural zeolites was established.

The adsorption rate of arsenate (As(V)) was higher in all the studied cases. For natural zeolites the adsorption of arsenate (As(V)) was 16% compared to 5% for arsenite (As(III)) adsorption. This behavior was replicated in the three types of zeolites. The results of arsenite and arsenate removal are shown in Figure 4.

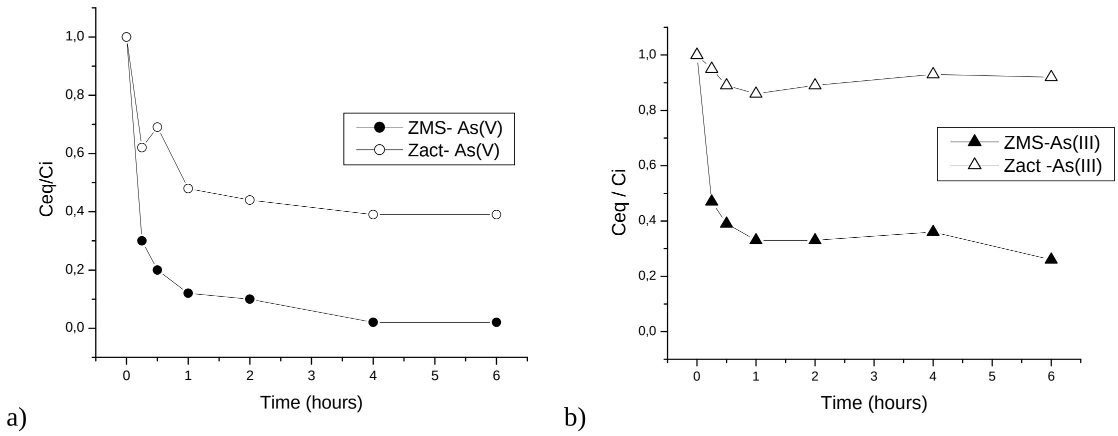



Figure 4. Adsorption of: 4a) arsenate and 4b) arsenite, by activated zeolites (Zact) and modified zeolites (SMZ). Initial arsenic concentration: 100 mg/L, solid-liquid ratio 1:30 and contact time from 15 minutes to 6 hours.

The results shown in Figure 4 show that arsenate was adsorbed by both kinds of pre-treated zeolites, activated and modified zeolites. In both cases the adsorption was more than 50 % and the highest value was 90 % when modified zeolites were used. These results were obtained when natural zeolites were activated before the modification process.

Concerning arsenite removal, this compound was only adsorbed significantly by the modified zeolites, SMZ-ODA reaching 70 % compared to 15% when using activated zeolites. These results support the fact that the most important mechanism for arsenite exchange in zeolites occurs when cationic surfactants are modified.

## Stage 2: Applied Research Zeolites as Multi-Adsorbent Material

In stage 1 the modification process for obtaining modified zeolites with an adsorption capacity of different oxyanions from aqueous solutions was established. The modified zeolites' capacity to adsorb different types of pollutants was analyzed in the second stage. Among the pollutants As(III) and As(V), molybdenum, selenium and sulfur (sulphate) and cations like: copper, nickel, and lead, among others, were considered. All these pollutants are frequently found in wastewaters from the mining industry.

According to the analysis of the modification process, the modification process only occurred on the surface of the zeolites and the sorbent maintained the ability to adsorb cations in the main channels of its structure. In order to prove this assumption an experiment was performed comparing the adsorbing capacity of different pollutants, individually and together in a synthetic solution. As can be seen in Table 2, two tests were performed. First a stock solution considered As(III), As(V), molybdenum, selenium, sulphate, copper, nickel and lead individually, and then all the elements were mixed with the modified zeolites for 2 hours. The capacities obtained are shown in Table n°2.

Table n°2. Ion adsorption capacities of modified zeolites

| Analite | Maximiun Adsorption capacity in mg/g in individual stock solution | Maximiun Adsorption capacity in mg/g in mixture stock solutions |
|---|---|---|
| Arsenite | 3 | 1.5 |
| Arsenate | 10.3 | 6.5 |
| Molybdate | 28.8 | 12 |
| Sulfate | 5.1 | 2 |
| Copper | 12 | 1.5 |
| Zinc | 13.5 | 2.1 |
| Lead | 20.2 | 4.5 |

Table n°2 shows that all the capacities obtained for the mixed solution were minor in comparison to the individual tests. However, the modified zeolites show their ability to adsorb both oxyanions and cations at the same time, demonstrating that the modification does not affect their natural capacity for cationic exchange.

### Stage 3: Applications of Modified Zeolites in the Copper Mining Industry

The main purpose of this project was to develop an effective wastewater treatment using activated and modified zeolites, specifically for effluents generated in the mining industry. In order to achieve this, several tests in continuous flow were conducted using modified zeolites for the treatment of three different effluents[10]. The main results obtained from these feasibility studies would show where the application of the ZEOTREAT technology would be most cost-effective.

The Zeotreat technology was tested in the treatment of different types of wastewaters from copper mining. In figure 5 its shown a diagram for the generation of wastewaters in different parts of the mining process and is shown in those effluents to which ZEOTREAT technology was applied.

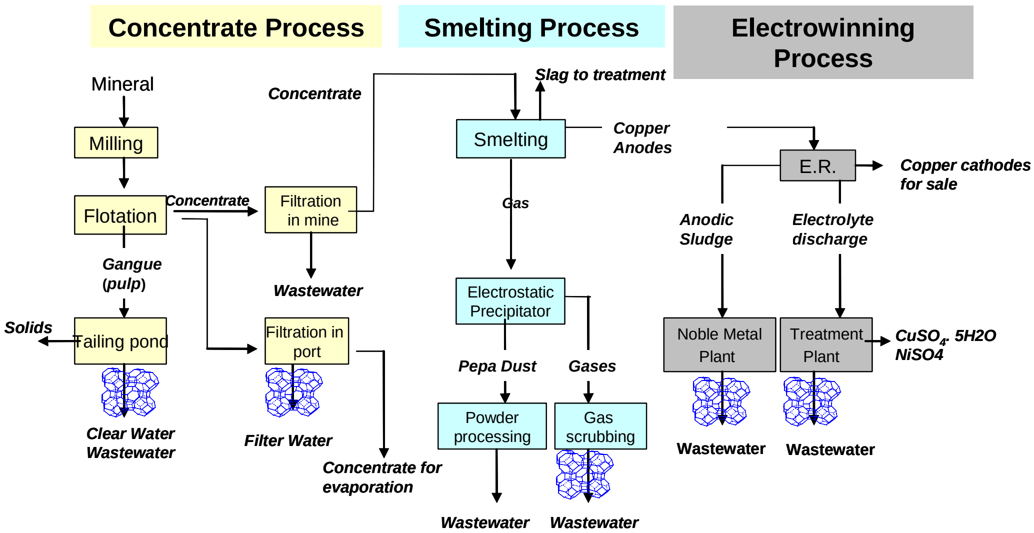



Figure 5. Scheme of mining process and generation of different wastewaters.

The main applications were in the treatment of clear waters from tailing ponds, in wastewater from filter processes and in acid wastewaters from the smelting process, obtaining results as described below:

- Clear waters from tailing ponds. The molybdenum was substantially removed and reached the required levels, while the sulphate rapidly saturated the modified zeolite
- Water from filter processes. The main pollutants removed were copper and molybdenum reaching removal rates close to 99 % in both cases.
- Acid waters from gas washing in the copper smelting process. In this case the wastewaters were shown to require pre-treatment before applying the Zeotreat technology because of the high concentrations of metals, arsenic and sulphate present. Removal rates of both forms of arsenic, As(III) and As(V) reached 80 %.

In general, the results obtained show that the initial concentrations of the contaminants in the wastewaters are a fundamental factor for the efficiency of the treatment. In the presence of high concentrations of pollutant, the adsorbent was rapidly saturated and had to be regenerated more often, which makes the treatment less cost effective. This was the case for both tailing clear waters and gaswashed acid water treatments. In the case of wastewaters from the filter process, the removal rates of molybdate and copper were over 99% and this result favors scaling-up.

### Stage 4: Scaling Up Zeotreat Technology

The final stage of this research included the validation of the ZEOTREAT technology in a pilot scale study performed during a two month period in one of Chile's biggest filter plants. With all the results and gained experience in stage 3 suggested that the best applications form the Zeotreat technology was treatment of wastewaters from filter plants.

The ZEOTREAT technology pilot plant was designed and implemented by Fundación Chile and financed by FONDEF [11] (see Figure 6).

Figure 6. ZEOTREAT technology pilot plant

The pilot plant included two columns embedded with zeolites, the first with activated zeolites for copper removal and the second with modified zeolites for molybdate removal. Each column contained 250 Kg of adsorbent material which is ten thousand times the mass used in laboratory scale (25 g). The pilot plant was housed in a container.

According to the results obtained in the pilot study the ZEOTREAT treatment, using activated and modified zeolites, proved that it can effectively adsorb copper and molybdate, reaching removal rates of over 99%. In table n°3 a full result its shown.

Table 3. Results of treatment with Zeotreat technology

| Parameter | Units | Initial Concentrations | Partial treatment (Stage 1) | Final treatment (stage 1 + 2) |
|---|---|---|---|---|
| Aluminum | mg/L | 30 | 0.2 | <0.1 |
| Boron | mg/L | 3.5 | 3.6 | 3.2 |
| Cadmium | mg/L | 0.01 | <0.01 | <0.01 |
| Calcium | mg/L | 538 | 182 | 493 |
| Copper | mg/L | 0.76 | 0.05 | 0.04 |
| Iron | mg/L | 0.92 | <0.05 | 0.64 |
| Lithium | mg/L | 0.7 | 0.3 | 0.6 |
| Magnesium | mg/L | 27.3 | 23.2 | 35.5 |
| Manganese | mg/L | 0.1 | 0.23 | 1.03 |
| Molybdenum | mg/L | 4.95 | 4.05 | <0.01 |
| Lead Total | mg/L | 0.04 | <0.02 | 0.05 |
| Potassium | mg/L | 62.4 | 8.8 | 12.5 |
| Sodium | mg/L | 664 | 2680 | 870 |
| Sulfate | Mg/L | 2288 | 2293 | 279 |
| Zinc | mg/L | 0.12 | 0.13 | 0.7 |

The ZEOTREAT technology was selective to cation or anion adsorption, in the first stage of the wastewaters treatment only copper was reduced. In the second stage molybdate was eliminated. These results were replicated in two cycles performed obtaining 95% and 75%, respectively. The activated zeolites had a higher copper adsorbing capacity compared to the molybdate adsorbence capacity of the modified zeolites.

In addition, sulfate was reduced in the second stage from 2288 mg/L to 279 mg/L. This parameter was not considered in the global treatment because for this specific application the sulfate level for discharge to sea is not regulated by national law.

Another relevant advantage is the possibility of recovering copper and molybdenum from eluates solution generated at the regeneration process.

The liberation and increase of manganese after the treatment was observed. However, this happens only in the first volume of the wastewater treated and could be avoided if a efficient first activation and modification process is performed.

The costs obtained for the integral treatment of wastewaters coming from filter plants varied from U$1.25 to U$1.70 per cubic meter, depending on the initial concentrations of copper and molydate present in the wastewater.

Finally, an excellent correlation between the laboratory and pilot scale, over 95%, was obtained for molybdate and copper removal. See Figure 7.

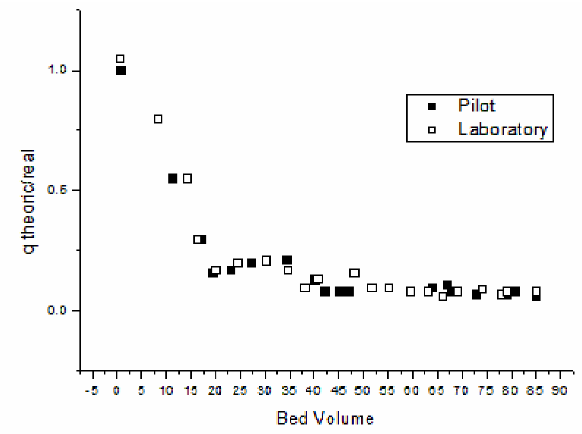



Figure 7. Molybdate adsorption capacities by modified zeolites, in laboratory and pilot scale studies

With these results the design and cost evaluation of the ZEOTREAT technology can be made at full scale.

## 4. CONCLUSIONS

The family of activated and modified zeolites that were obtained show that they are fully capable of efficiently adsorbing oxyanions of molybdenum, arsenic and sulphur. The developed technology also demonstrated its ability to remove several types of pollutants that are present in complex matrices (Cu, Fe, $SO_4^{2-}$, Mo, As(III), As(V)), achieving the removal levels required by regulatory demands.

The results had a 94% rate of reproducibility from laboratory to pilot scale providing encouragement for the scale-up to industrial application.

The use of the ZEOTREAT Technology for the treatment of mining wastewaters is a competitive solution for diluted wastewaters such as filter waters where no other technology has proven to be cost-effective.

The performance of this technology is currently being enhanced and improved with the use of new materials that have significant comparative advantages, including:

- Low-cost investment
- High removal capacity
- Life expectancy from 3 to 10 years
- Great versatility, efficiency and selectivity
- Simplicity of operation
- The use of small spaces
- The use of common reagents for the regeneration of the material
- No sludge generation and low volumes of eluates produced

In this new line new applications have been developed for the treatment and upgrading of wastewater from: agribusiness, water treatment plants, chemical industries, among others.

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