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High efficiency of tuff quarrying residuals and their associated mordenite for adsorbing chromium and lead from aqueous solutions

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Abstract

In this study we present a dacite quarrying material susceptible for use as a lead and chromium adsorber in aqueous systems. Its efficacy in adsorbing these heavy metals reached >97% and ~95% for chromium and lead, respectively. Given that the presence of mordenite is often initially interpreted as the principal factor associated with this high adsorbing efficiency, sample treatment via a phase separation process was performed in order to obtain a material with a high concentration of mordenite, on the other hand, in order to planning the experiments we used an experimental design methodology and ANOVA analysis method. Subsequently, the resulting material only showed slight incremental increases in adsorbing capacity. Thus, the quarrying material appeared to be a good candidate for use, as received from mining exploitation.

Keywords: Ash-fall tuff, mordenite, residuals, adsorbents, heavy metals.

1. Introduction

Zeolites are best-defined as aluminosilicates with a framework structure enclosing cavities occupied by large ions and water molecules, both of which have considerable freedom of movement permitting ion exchange and reversible dehydration; chemically, they are related to feldspars but have much more open structures [1].

Mordenite is one of the more widespread members of the zeolites group, naturally occurs in rather large quantities in some altered vitreous tuffs [2].

Its morphology is typically characterized by a predominant fibrous habit, although the occurrence of blocky reniform aggregates is not rare [3]. Mordenite crystallizes on the orthorhombic spatial group *Cmcm*, with parameters a= 18.13 Å, b= 20.5 Å, c= 7.52 Å, and it features an ideal chemical composition, $Na_8Al_8Si_{40}O_{96}\cdot 24H_2O$ [4]. Sedimentary deposits of mordenite are present in several countries, especially in Bulgaria, Hungary, Japan and United States; quarried material is generally substantial [5]. Apart from generic applications in the fields of agriculture and building industry (as dimension stone), uses are known as sorbent and molecular sieve [5].

The structure of zeolites is characterized by a framework of linked tetrahedral, each containing four oxygen atoms at their apices, surrounding silicon or aluminum [6]. This framework contains open cavities in the form of channels and cages, which are usually filled by H_2O molecules and extra-framework cations that are commonly exchangeable [6].

In the last decades, natural zeolites have found a variety of applications in adsorption, catalysis, building industry, agriculture, soil remediation and energy [7], but their use for environmental applications is gaining new research interests mainly due to their properties and significant worldwide occurrence, especially, application of natural zeolites for heavy metal removal in water and wastewater treatment has been realized and is still a promising technique in environmental cleaning processes [8] as reported in several studies [9-15]. From this point of view, their ion exchange property holds particular relevance, the ion exchange behavior of natural zeolites depend on several factors, including the framework structure, ion size and shape [8].

The discharge and widespread distribution of heavy metals into aquatic ecosystems has become a global matter of great concern over the last few decades because of their toxic properties [16,17]; Cr(III) for example, is a dangerous contaminant in the effluents that is originated mainly in the leather tanning industry and is well known for its toxic effects [18], but is worth noting that, although the hydrated Cr(III) ionic radius is the greatest among the heavy metal ionic species in aqueous solutions, some zeolites appear to be suitable materials that are capable of adsorbing ions due to their compatible pore-opening sizes [19]. Another metal ionic species that is associated with industrial water contamination, and which is also related to health-related toxicity that affects basic cellular processes and cerebral functions, is Pb(II) [20]. In this case, zeolites (such as clinoptilolite, ferrierite, and mordenite) have been modified to obtain their sodium and ammonic forms, and they were reported as good candidates as Pb(II)-adsorbers in waste waters, especially in sodium form [21, 22].

The main goal of this study is to recover natural mordenite from a dacitic pyroclastic rock obtained from the Tezoantla mine (Hidalgo, Mexico), and to subsequently evaluate its capacity to adsorb Cr(III) and Pb(II) in aqueous solutions. A series of controlled experiments were designed in order to determine the optimum levels of concentration, time, pH and stirring rate to remove these cationic species.

2. Materials and methods

2.1 The starting material

The zeolite-bearing rock used here has originally been exploited as dimensional stone and it was extracted from the Tezoantla mine, sited at Mineral del Monte, Hidalgo, Mexico (N20°07' W098°41', and 2660 meters above sea level). This raw material is an extrusive igneous rock conformed by compacted ash-sized pyroclasts or ash fall tuff. Its aspect is earthy; it presents a fine-grained and slightly laminar texture, and is opaque with a milky-white color. In hand sample, it exhibits subhedral quartz and feldspar fenocrystals, a small quantity of ferromagnesian minerals, and some oxides with a dark greenish color that resulted from weathering processes.

From the cutting of the dimensional stone, which is essentially destined for use in construction, a great volume of zeolite-bearing quarrying material is generated. Namely, following a mass balance analysis, a total volume of at least 50% of the removed material is wasted during the extraction and cutting processes. Samples were collected from the wasted material that originated in the workbench area near the mining surface, and they were transported to the Geochemistry Lab of the Autonomous University of the Hidalgo State where they were crushed and sieved. Following that, they were powdered with an agate mortar and pestle for chemical and mineralogical analyses.

2.2 Whole-rock chemistry

Knowledge of the samples' chemical composition is essential to elucidate the nomenclature of this volcanic material. For this purpose, a major elements analysis in one powdered sample of tuff was performed by FUS-ICP (fusion-inductively coupled plasma with metaborate/lithium tetraborate) in ActLabs (Toronto, Canada), and the corresponding results were plotted in a TAS diagram [23]. The results revealed that the rock is a dacite. Additionally, a trace elements analysis was also performed in ActLabs [24] to primarily evaluate the rock's concentration of lead using TD-ICP (total digestion–inductively coupled plasma) and chromium using INAA (instrumental neutron activation analysis). Even though a complete analysis of major and trace elements was performed, in Table 1 are only the results concerning to lead and chromium, both elements were selected because these constituted the focus of the sorption experiments. The presence of these elements fell below the detection limit, which allowed us to consider this dacite as a good target material to evaluate its lead and chromium sorption capability. Table 1 also summarizes the rest of chemical analyses results.

Table 1. Chemical composition of the Tezoantla sample

Compound/Element	**SiO_2**	**Al_2O**	**Fe_2O_3(T)***	**MnO**	**CaO**	**Na_2O**	**K_2O**	**TiO**	**Cr**	**Pb**
Result (wt% / ppm)	70.81	11.88	1.29	0.03	0.14	2.72	2.01	0.11	<1	<5

* Total iron

2.3 Phase identification

The identification of mineral phases occurring in the powdered samples of the tuff was carried out from monodimensional I/2θ diffraction data. The equipment used was a Rigaku Dmax 2100 diffractometer, with the source operating at 20 kV and 30 mA in a reflection mode. The copper Kα1 (λ1=1.5406 Å) and Kα2 (λ2=1.5443 Å) doublet wavelength was chosen for all the experiments. Asymmetric configuration was selected by fixing the incident angle at 2°. The combination of the reflection mode and the asymmetric configuration is usually referred to as grazing or glancing X-ray diffraction (GIXRD) to differentiate it from the classical or standard symmetrical Bragg–Brentano powder X-ray diffraction (PXRD) method. A primary parallel beam was used to achieve higher intensities on an irradiated area of approximately 1 cm^2. A scintillation punctual detector collected the intensity data. The experiments were performed at room temperature, in a 2θ range between 1.00° and 39.74°, a step-size of 0.02°, and a step time of 0.7 s/step. The first diffraction pattern was obtained on an apparently randomly-oriented powdered (as received from the lab) sample of tuff without additional treatment. This experiment serves to identify and semi-quantify the mineral phases that originally occurred on the rock. The powder was deposited into a glass-slide holder (with a 15×12×1.5 mm vessel) and it was slightly pressured with another slide in order to create a completely planar surface. The pattern (Fig. 1) indicates the presence of quartz (PDF 00-046-1045) and mordenite (PDF 00-029-1257). Semi-quantification was carried out via the reference intensity ratio (RIR) method [25, 26], and this resulted in a ~70% weight of quartz and a ~26% weight of mordenite (an error bar of 5% was assigned to these mineral percentages). Any additional mineral phases were not detected, although at a low 2θ, an important increment of the peak-shaped background intensity at low 2θº indicates a minor presence of non-oriented clays. Equally, a background intensity increment that falls below the principal peaks of quartz at a range of 20°–30° 2θ is evidence of the presence of some amorphous fractions, probably due to a trace of opal A. Nevertheless, in both cases, either the non-oriented clays or the opal are present at a percentage of <3 wt %.

In order to evaluate the presence of possible traces of clays, further diffraction experiments were performed on oriented aggregate samples. Concomitantly, we expected that the preferred orientation treatment, as previously reported [27] and adapted for our sample types, was an effective method that could be used to isolate and concentrate mordenite from quartz.

Given that preparations known as oriented aggregate mounts are the result of the separation of plate-shaped particles (e.g. phyllosilicates) from the bulk sample via centrifugation, decantation or evaporation processes was applied to a water–powdered sample mixture. The product of these processes is a thin layer of particles that lies flat in a parallel arrangement over a substrate, these mounts enhance the intensity of the basal planes, which are characterized by long spacing in a diffraction pattern because the most of the planes are oriented parallel to the horizontal plane of the sample holder [28]. In this sense, and taking into account the low density of the mordenite (2.1–2.2 g/cm^3), our oriented aggregate mounts were made from a water suspension of Tezoantla tuff in a 500 mL glass column. This suspension was manually stirred, and afterwards, we let it rest for 15 minutes. After that, the floating fraction was removed from the column and deposited over a glass substrate; the evaporation process was conducted at room temperature, where the water remnants force the mineral particles to precipitate, lying flat over the substrate. This step was repeated 7 additional times by progressively increasing the floating time in increments of 15 minutes, reaching a maximum of two hours. We realized that after repeating the same process 4 times, we could obtain oriented aggregate sample mounts that were thick enough to minimize and control the interference of the substrate in the diffraction patterns.

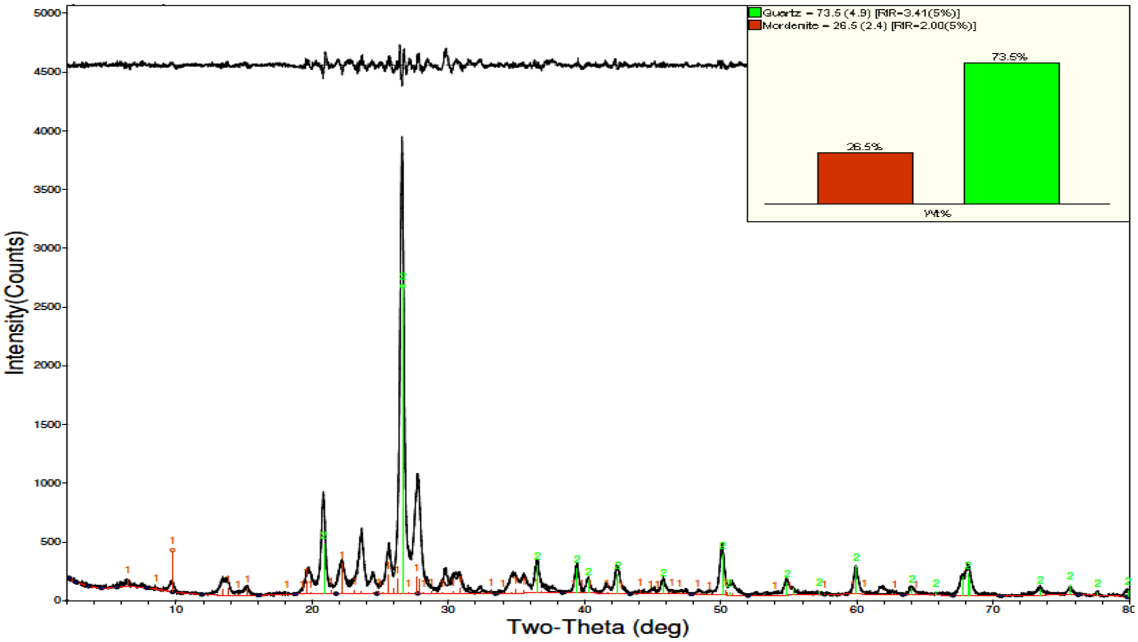

Figure 1. X-ray spectra of the Tezoantla sample

Figure 2 shows the GIXRD patterns of 7 mounts constructed at different floating times: 15, 30, 45, 60, and 120 minutes, and additionally at 24 and 52 hours. The exploitation of these patterns revealed two important aspects in the characterization of the material: i) that there was a presence of a Montmorillonite – 22 Å (PDF 00-029-1499), which was very evident, and this was an indicator of the effectiveness of the oriented aggregate mounts on the identification of clay traces; and ii) the technique applied here to obtain the oriented aggregates was also very effective in isolating and concentrating the mordenite, which occurred within the context of a very small percentage of quartz that remained in the sample. At 30 minutes, the concentration was almost invariable with respect to the concentration obtained at only 15 minutes.

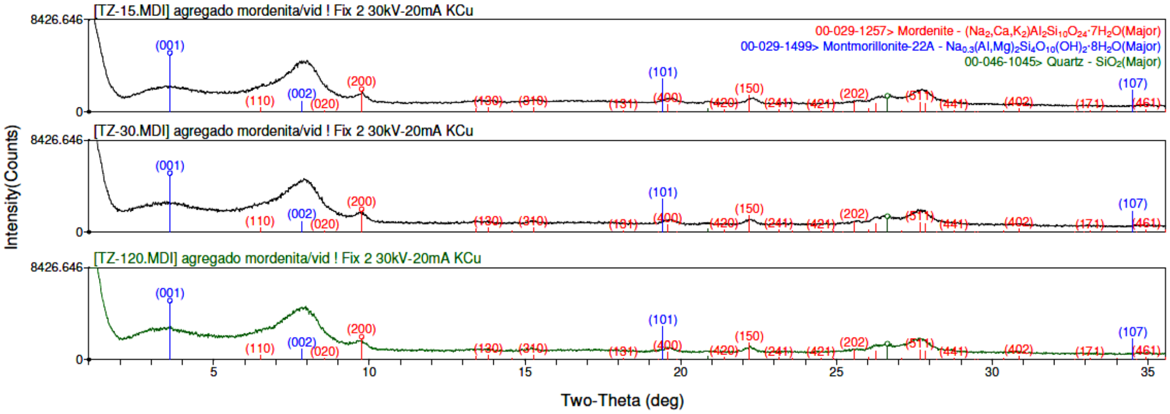

Figure 2. X-ray spectra of the oriented aggregate mounts for the different floating times (15, 30, and 120 minutes)

2.4 Bulk recovery

Adapting the oriented aggregate technique for the zeolite recovery, a suspension was prepared in a 2 L test tube after mixing distilled water and 100 g of Tezoantla tuff. The suspension was constantly stirred for 15 minutes (1100 rpm) and it rested for 30 minutes, which is the minimum amount of time that was established in DRX for oriented aggregates. After this time, 400 mL was collected from the top of the suspension and deposited in flat pans at room temperature to completely evaporate the water. This procedure was repeated until 300 g of zeolite were obtained, which served as the controlling mineral phase.

2.5 Experimental design

Table 2 shows the experimental design, which was characterized by ordering an orthogonal array consisting of 4 factors and three levels across 9 tests [29]. Every test was performed three times with same experimental conditions for each independent lead and chromium solution. The values of the 4 controlled variables and their respective levels are summarized in Table 3.

Table 2. Matrix of the experimental design

Experiment	**A**	**B**	**C**	**D**
1	1	1	1	1
2	1	2	2	3
3	1	3	3	2
4	2	1	2	3
5	2	2	3	2
6	2	3	1	1
7	3	1	3	1
8	3	2	1	2
9	3	3	2	3

Table 3. Controlled variables and levels in the orthogonal array

Variable/Level		**1**	**2**	**3**
A	Concentration (mg/L)	10	20	30
B	Time (minutes)	10	20	30
C	pH	4 ± 0.2	6.3 ± 0.2	8.3 ± 0.2
D	Stirring rate (rpm)	80	115	180

2.6 Preparation of experiments

In order to evaluate the results extracted from the variable optimization process at the laboratory level, a huge quantity of recovered zeolite-bearing material was used. Nine chromium and lead 25 mL solutions were prepared, maintaining the conditions evaluated in the experimental design. The solutions were mixed with 0.5 g of the powdered tuff in Erlenmeyer flasks.

In each experiment, an aliquot of 20 mL was acidified with 2% HNO_3 for analysis using the ICP technique.

3. Results and discussion

3.1 Batch experiments

The results are shown in Table 4; from them, we can infer that the best percentages of retention for both elements are associated to the experiment number 7: 97.29% and 90.6% for chromium and lead, respectively. However, regular values of approximately 20% in the variance coefficients are obtained. Values lower than 14% are understood as experiments with an acceptable accuracy, whereas those higher than 20% are classified as experiments with not many precission [30]. Accordingly, it was determined that the best retention percentages are obtained upon conditions of experiment number 7, though in this case the accuracy of the estimation is low. Unlikely, experiments 1 and 2 clearly present acceptable values of accuracy for the chromium determination (retention values higher than 90%), as well as the experiment 1 and 4 for lead, with percentages above 80%.

An analysis of variance (ANOVA) was performed using the software *Analysis of variance using Taguchi Methods ANTM 003071, version 2.5*. Subsequently, the combination of A3B3C1D3 (Concentration 30 mg/L; 30 minutes; pH 4±0.2; 180 rpm) and A3B2C1D1 (Concentration 30 mg/L; 20 minutes; pH 4±0.2; 80 rpm) were found to be optimal for chromium and lead, respectively (Fig. 4). It is worth noting that any of these combinations were not previously tested, so it was necessary to perform further experiments using both quarry rock and recovered zeolite.

According to the ANOVA analysis, the concentration is the most influent variable in the process. The differences between these combinations can be explained in terms of time and agitation rates. On the other hand, they present coincidences in initial concentration level, as well as the pH. In terms of pH, the most favourable or optimum result was obtained for both metals at the lowest level of this variable in the experimental design (4 ± 0.2); this is in agreement with the statement reported by other authors who related low pH's with the mobility of ionic species (M^{n+}) that concomitantly promotes adsorption mechanisms [31].

Table 4. Results for the ICP analysis (the concentration of the remaining metal in the solution)

Experiment	**Cr (mg/L)**	**Cr (%CV)**	**Cr retention (%)**	**Pb (mg/L)**	**Pb (%CV)**	**Pb retention (%)**
1	0.85 ± 0.09	10.59	91.51	1.99 ± 0.13	6.53	80.13
2	0.67 ± 0.06	8.96	93.26	1.45 ± 0.35	24.14	85.54
3	1.34 ± 0.30	22.39	86.60	1.83 ± 0.78	42.62	81.71
4	1.43 ± 0.17	11.89	92.83	2.16 ± 0.19	8.80	89.22
5	1.10 ± 0.47	18.02	94.48	3.33 ± 0.60	18.02	83.34
6	1.54 ± 0.17	18.75	92.30	2.24 ± 0.42	18.75	88.80
7	0.81 ± 0.19	23.46	97.29	2.82 ± 0.56	19.86	90.60
8	4.76 ± 1.18	14.29	84.14	4.34 ± 0.62	14.29	85.54
9	4.39 ± 0.86	36.45	85.38	2.99 ± 1.09	36.45	90.04

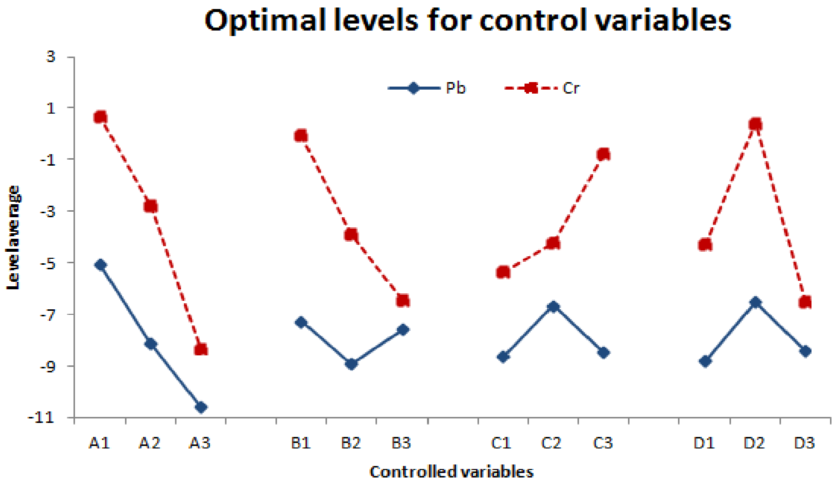

Figure 3. Optimal levels for each variable in terms of Pb and Cr retention

In metallic ions as Cr and Pb, the influence of pH on the adsorption process is explained via the oxidation, within the pH range 5.5 - 6, from trivalent to hexavalent chromium, specie with the highest toxicity. Otherwise, lead is hydroxilized and the resulting compounds precipitate or sedimentate, affecting the adsorption process [32, 33].
It is worth to remark that any optimum resultant combination have not been initially considered on the design matrix, so in order to verify the experiments, some further experiments were performed on both the natural tuff, as well as the recovered zeolite.

3.3 Batch experiments to confirm the retention values

The final results with their optimal conditions are summarized in Table 5. Further experiments at same experimental conditions and number of tests were performed. The preparation processes that were used to analyze these samples via ICP were also maintained.
The retention percentages of tuff were slightly increased with respect to the ANOVA analyses, as they were 97.83% and 95.44% for chromium and lead, respectively. For the zeolite, the behavior was similar: retention percentages reached 99% and 96% for chromium and lead, respectively.

Table 5. Heavy metal concentration results during the checking tests

Cr (mg/L)			
Natural tuff	Retention (%)	Natural zeolite	Retention (%)
0.22 ± 0.12	97.83	0.06 ± 0.01	99.38

Pb (mg/L)			
Natural tuff	Retention (%)	Natural zeolite	Retention (%)
0.46 ± 0.11	95.44	0.40 ± 0.07	96.01

Conclusions

A separation and concentration process was successfully applied on a quarry zeolite-bearing material, leading to approximate concentration values of 95%. This zeolite-enriched material was obtained with the main goal of being able to test it on heavy metal (Cr and Pb) retention experiments using aqueous solutions. Although the retention values were very high for the material enriched in zeolite, it is important to mention the high values that were also obtained for the initial material, which was a volcanic tuff from waste quarry material. This latter point leads us to consider that volcanic rock is a good candidate for exploitation as a material characterized by heavy metal retention.

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