Diatoms and Their Capability for Heavy Metal Removal by Cationic Exchange

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Abstract: This work shows the physicochemical behavior of two different diatoms from the country of Mexico (State of Jalisco and Hidalgo) with similar compositions. These were used to eliminate toxic cations from a synthetic solution containing 5.270 mg As^{3+}/L; 4.280 mg Ag^+/L; 3.950 mgNi^{2+}/L; 4.090 mg Cr^{6+}/L; and 4.081 mg Pb^{2+}/L. These diatoms were used as filters, and the quantity of cations remaining in the solution after filtering was measured. According to the most important results found, for the recovery of metals, both minerals achieved arsenic, silver, lead, and nickel recoveries up to 95%, and lower than 10% for chromium. This could be due to the absence of an environment to reduce Cr^{6+} to Cr^{3+}. On the other hand, it was observed that there was no selectivity during the recovery of the other cations present in the solution. According to efficiency of interchange, the mineral from Hidalgo is slightly better than the mineral from Jalisco for the removal of arsenic, lead, and silver. For nickel, and particularly Cr^{6+}, the efficiency is higher for the sample from Jalisco.

Keywords: diatomite; ionic exchange; metals removal; heavy metals

1. Introduction

Diatomite is a siliceous rock of sedimentary origin that is inert and of low toxicity that shows small quantities of associated inorganic compounds, such as aluminum, iron, ammonium, alkali metals and other minor constituents [1]. It is also formed by crystalline aluminum silicates of tetrahedral structure linked among them, which share oxygen atoms. The elemental cell structure consists of tetrahedral molecules of SiO_4 and AlO_4 arranged in such a way that each oxygen atom is distributed between two adjacent tetrahedrons. Diatomite is also composed mostly of the fossilized fragments of diatom algae [2,3]. It is basically microscopic unicellular marine algae with varied shapes and sizes. The algae are composed by a transparent cellular wall, with a translucent outer layer of crystal-like silica [4], and an inner layer of pectin, with a chemical composition of the diatoms' walls of 96.5 wt. % of silica and 1.5 wt. % of sesqui-oxides.

The minerals also have properties similar to clay, where in some cases the thermodynamic swelling could be related to the tendency of the charge-balancing counterions to hydrate the hydrophilic interaction between the clay surface and water, and the strength of the interaction between the clay surface and the counterion [5]. On the other hand, some researchers have disclosed that for clay

swelling to occur, water molecules must pass from external regions (i.e., external surfaces, internal surfaces, and micropores) to the interlayer gallery, passing between all clay edges. It has been determined that, in contrast to the chemically-inert basal plane, the edges of particles are extremely reactive [6–9], containing both Brönsted acid and base groups. Other authors [9–11] have reported that the reactive nature of clay layer edges has been implicated in catalysis reactions, such as polymerization.

Other studies have evaluated different types of materials, such as fibrous absorbents, resins, polymeric anion exchangers, ligand-doped conjugate absorbents, mesoporous absorbents, among others, for the removal of arsenic [12,13], phosphorous [14,15], and lead [16–19]. This has led to good results, not only for removal of these metals, but also in the reuse of exchangers. This last point is of importance for the cost efficiency of the method and material to be used in the removal process.

Industrially, diatomite is used in a variety of fields, and has different names depending on its purity or the region of origin. Diatoms are widely used as filters in diverse branches of industry, such as in water filters, filters for the elaboration of beer and wine [2], filler additive, absorbent additive, and as a soft abrasive. There are few research works related to the use of diatoms for the treatment of wastes for the recovery of metals. This work will evaluate the capacity of this material to remove heavy metals from solution.

2. Methodology

The material used in this work was sampled in the mining region of "El Barqueño" in the state of Jalisco, and the other in the community of "Loma Larga" in the county of "Acatlán", in the state of Hidalgo, both in the country of Mexico. For characterization techniques, it was necessary to prepare the sample to particle sizes lower than 100 μm, and then characterize by the following analytical methods: X-ray diffraction conducted with an INEL Diffractometer model Equinox 2000 located at the Autonomous University of the State of Hidalgo (UAEH), Mexico. The MATCH database was used to index the spectra. The quantification of elements contained in samples was carried out by inductively-coupled plasma spectrophotometry using a Perkin Elmer model 2100 (located at UAEH). The morphology of samples was obtained using a scanning electron microscope, JEOL model JMS 6300 (located at UAEH) with a voltage of 30 keV and equipped with an Energy Dispersive Spectrometer of X-ray EDS detector.

For the analysis of particle size, a 0.3 g sample was dissolved in 125 mL of water, and then analyzed in a particle size analyzer by laser diffraction; model LS-13320 (located at UAEH). The porosity was measured using porosity measuring equipment by BET Micrometrics, model ASAP 2020, carried out with 1 g of sample. Finally, IR spectrophotometry was obtained with Perkin Elmer Flouries equipment.

In addition, water content was calculated by difference in weight, using a 100 g sample and then placing it in a furnace at 350 °C for one hour. After that, the sample was removed from the furnace, it was cooled until it reached a temperature of 25 °C, and was finally reweighed to calculate the difference and the percentage of water content.

An atomic absorption spectrophotometer (AAS) was used to evaluate the exchange capacity of metals during absorption proofs. Samples included nitrates of Ag^+, Ni^{2+}, Pb^{2+}, As^{3+}, and Cr^{6+}. To determine if there was ionic exchange with the clay present in the diatoms, the sodium concentration in the water–diatom mixture was measured. Results indicated if sodium was present, and was compared with a pattern. A solution containing the mentioned metals was added in an average concentration of approximately 4 mg/L. For each test set, a calibration curve with patterns from 0.1 to 10 mg/L (including blank) was conducted to evaluate the amount of cation in solution before and after each proof. The two solutions having 5.270 mg As^{3+}/L; 4.280 mg Ag^+/L; 3.950 mg Ni^{2+}/L; 4.090 mg Cr^{6+}/L; and 4.081 mg Pb^{2+}/L were added to both diatoms separately (Diatom from Jalisco and diatom from Hidalgo), and left for one week to allow for permanent contact and exchange. At the end of the reaction time, the solution was filtered, and the corresponding measurements by AAS were made to obtain the concentration of each cation remaining in solution [20].

The removal efficiency (Er, amount of cation removed from solution) was calculated using the following formula:

$$E_r = 100\ (C_o - C_f)/C_o \qquad (1)$$

where, C_o is defined as the initial concentration of the metal of interest, and C_f is the metal concentration once exposed to diatom. The two samples were taken and the liquid was evaporated, adding 100 mL of water to the first sample and 100 mL of HCl at 0.1 mol/L to the second sample. It was allowed to stand for 5 days, and the concentration of the metal was measured.

3. Results and Discussion

The principal mineral species identified in the diatoms studied by X-ray diffraction are shown in Table 1. Results show that the majority species found was quartz. Other mineral species were also present in different amounts (Figure 1 for diatom from Hidalgo state). In Figure 2 (diatom form Jalisco), the diffraction pattern for natural diatom (D), calcined with flux diatom (D-C) and calcined without flux diatom (D-S) can be observed.

Table 1. Mineral species identified in the materials studied.

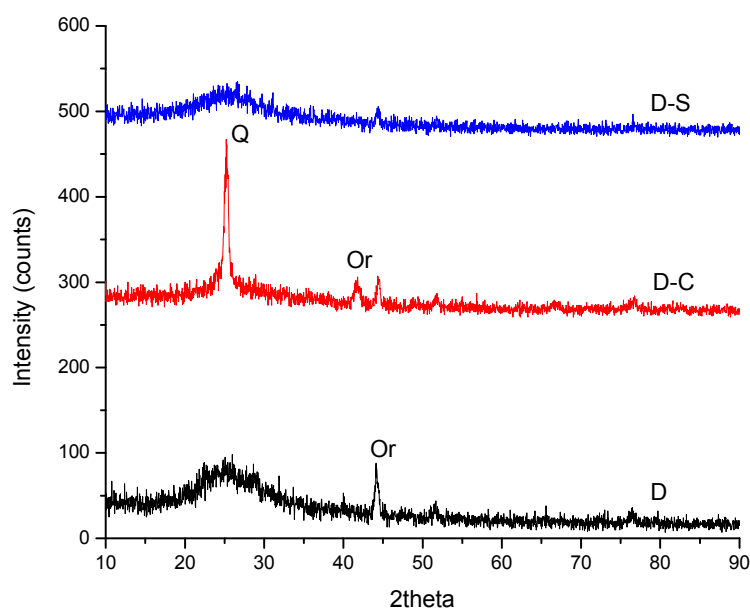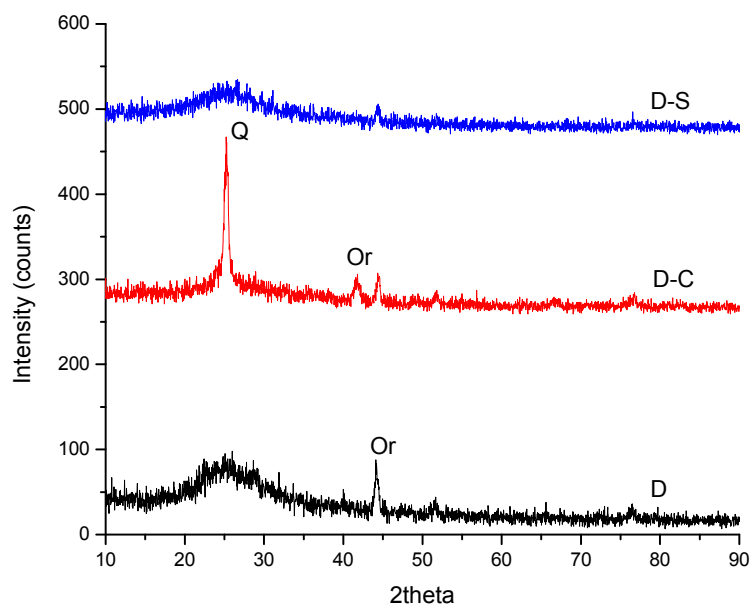| Origin	Mineral Species
Jalisco	Silica, Albite, Muscovite, Potassium Feldspar, Mogonita, and Andesite
Hidalgo	Silica, Albite, Muscovite, Potassium Feldspar, Mogonita, and Andesite

Figure 1. X-ray spectrum of diatom from the state of Hidalgo, Mexico (where Q is quartz and Or is Orthoclase).
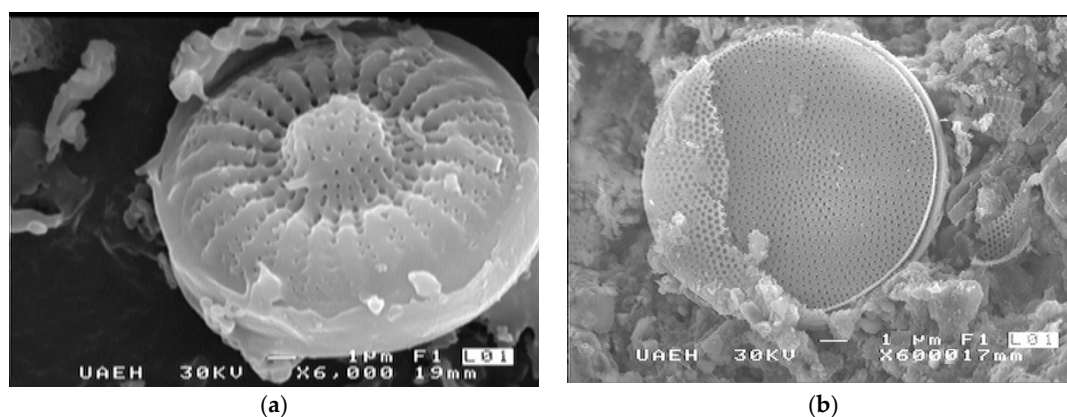
From the chemical analysis results, the principal elements present are Si, Al, K, Na, Ca, Fe, and Mg. Values that are associated to their respective oxides (Table 2) represent normal values for high-quality diatoms.

Table 2. Chemical compositions for the diatoms studied.

Origin	Treatment	Element % wt							
		SiO$_2$	Al$_2$O$_3$	K$_2$O	Na$_2$O	CaO	FeO	MgO	TiO
Hidalgo	Natural	70.0	11.63	2.41	6.10	0.85	1.95	1.79	0.50
	Calcined without flux	81.50	12.00	2.10	1.45	0.10	1.44	0.48	0
	Calcined with flux	82.00	11.15	1.96	2.82	0.13	1.646	0.51	0
Jalisco	Natural	93.58	3.03	0.92	0.24	0.11	1.81	0.40	0
	Calcined without flux	96.39	3.25	0.05	0.23	0.0	0	0.08	0
	Calcined with flux	94.49	2.90	0.7	1.75	0.07	0	0.09	0

Figure 2. X-ray spectrum of diatom from the state of Jalisco, Mexico (where Q is quartz and Or is Orthoclase).

The average size of diatom pores was also measured, where values vary from 1.5 µm to 7 µm as determined by scanning electron microscopy (SEM) for both diatoms. The morphology of this material can be observed in Figures 3–5.

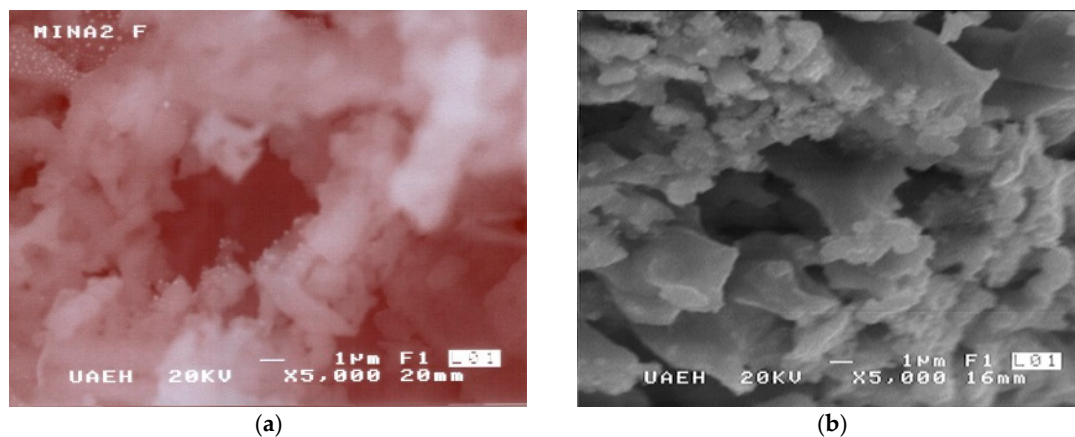**Figure 3.** Photomicrography of diatoms: (**a**) natural diatom from Jalisco; (**b**) natural diatom from Hidalgo.

| (a) | (b) |

Figure 4. Photomicrography of diatoms: (**a**) calcined with flux from Jalisco; (**b**) calcined with flux from Hidalgo.
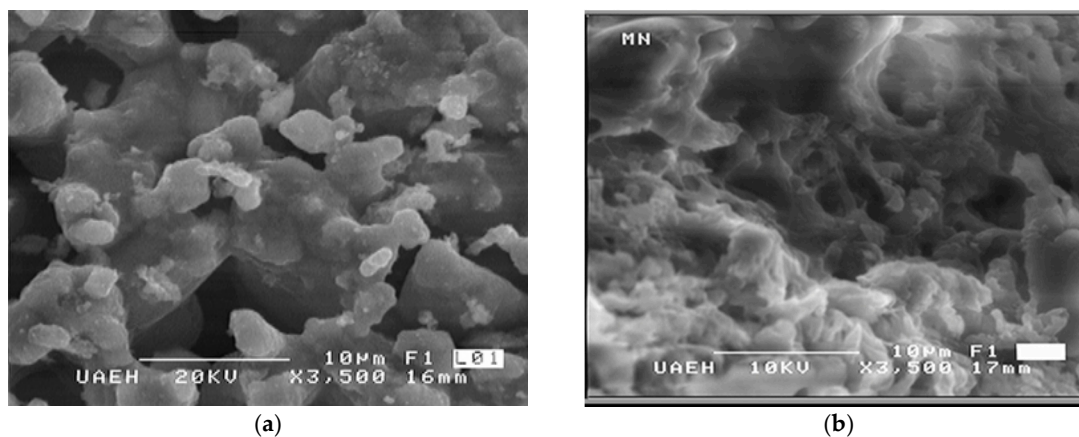

| (a) | (b) |

Figure 5. Photomicrography of diatoms: (**a**) calcined without flux from Jalisco; (**b**) calcined without flux from Hidalgo.

In the study of particle size, a bimodal granulometric curve was observed, and the maximum range shows a major percentage of retained material in particle sizes ranging between 12.99 and 22.73 μm for the diatom from Jalisco and from 12.87 to 22.51 μm for the diatom from Hidalgo, showing a retained weight ranging from 4–4.49% and from 4–4.48%, respectively. An average particle size of 17.18 μm for diatom from Jalisco, and 17.23 μm for diatom from Hidalgo was observed. Particle size with maximum percentages for both materials clearly demonstrates that the minerals correspond to a clay/silt material. Additionally, another maximum range of retained material was observed between particle sizes ranging from 39.78 to 63.41 μm, showing a retained weight in the range of 2.33 to 2.96% for diatom from Jalisco. For diatom from Hidalgo, the data showed 39.58 to 63.23 μm for particle size, with a retained weight of 2.30 to 2.92%. We can see that studied diatoms show mostly fine textures, and principally in particle sizes not larger than 40 μm. It is possible that residual material shows silicified and agglomerated particles (Figure 6).

According to results obtained for the determination of water content in the studied diatoms, it was found that water amounted to 4.2% for the material from Jalisco and 5.4% for diatom from Hidalgo. This is favorable because with low values, the diatoms have a higher absorption capacity. Water content is an important factor that promotes liquid absorption capacity in diatoms.

On the other hand, when diatom is calcined, the hydroxyl groups on the mineral surface are lost in the form of water, and a greater quantity of silanol groups are exposed (Si-OH). This improves its capacity to absorb liquids, due to the increasing pore size in both diatoms.
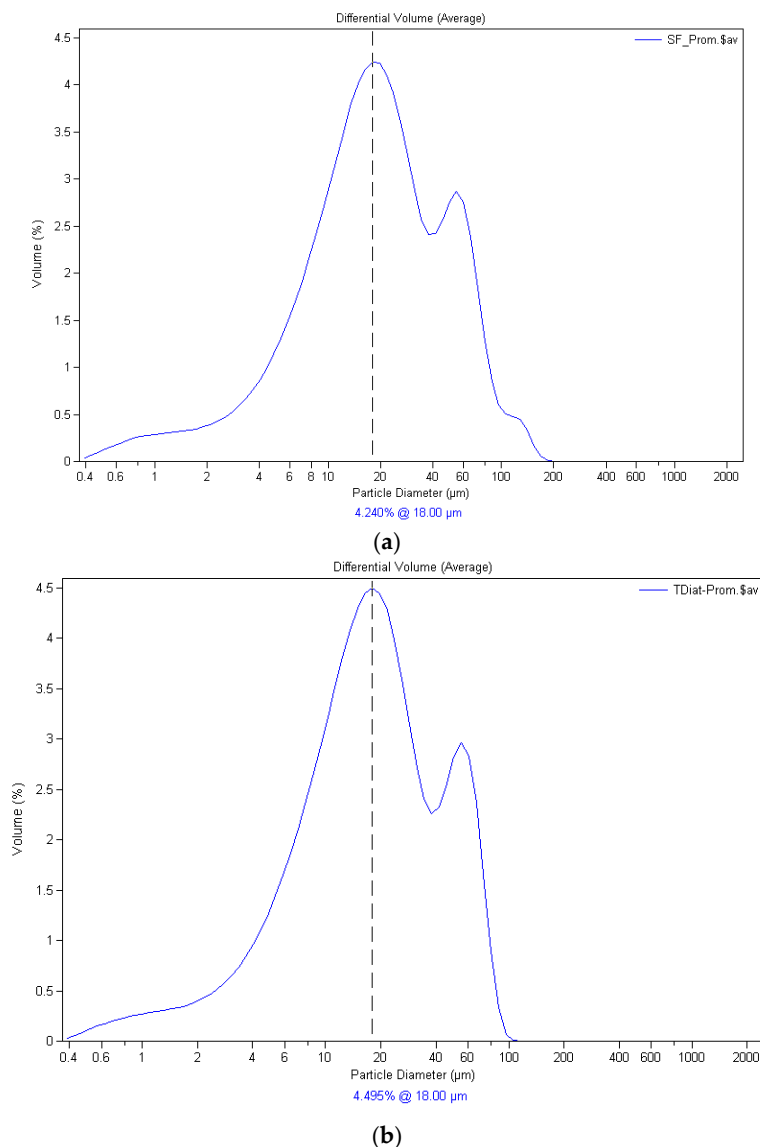
(a)

(b)

Figure 6. Particle Size: (**a**) diatom from Jalisco; (**b**) diatom from Hidalgo.

Figure 7 shows the Fourier transform infrared spectrometry spectra, where the position of the peaks was found for the natural diatom (D), calcined diatom with flux (DC), and calcined diatom without flux (DS). It was observed that all are coincident, only varying slightly in their intensity. This is evidence that siloxane groups (Si-O-Si) [20–23] can be formed during the calcination of diatoms, which was verified by elimination of the water and the increase in temperature. This results in a release of water, and the corresponding band to the vibrational modes of the OH groups (Si-OH and H-OH) of 3430 cm^{-1} is separated into two differentiated signals (3692 cm^{-1} from Si-OH, and 3432 cm^{-1} from H-OH). In addition to losing water, the band corresponding to the Si-O group of 1098 cm^{-1} decreased in intensity due to the loss of this kind of link. Other bands that decreased correspond to water (3432 cm^{-1} and 1638 cm^{-1}).

Table 3 shows the properties of the studied diatoms in their natural state, and calcined with and without flux. It is possible to observe that properties such as porosity, density, and compressive strength improve substantially after calcination versus that observed for natural mineral.
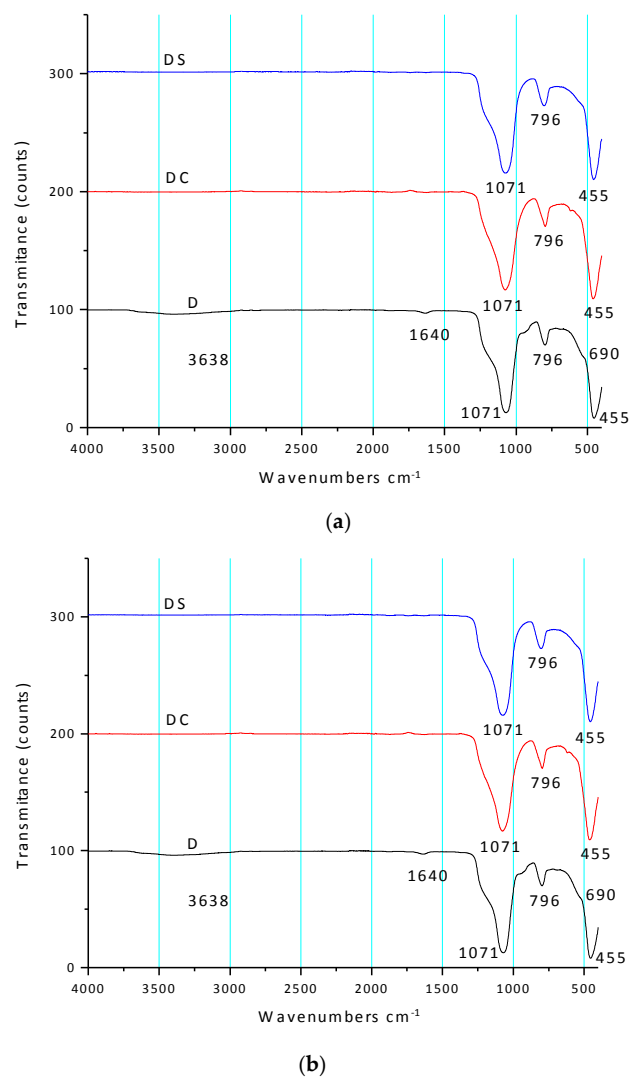
(**a**)

(**b**)

Figure 7. Fourier transform infrared spectrometry spectrums of (**a**) diatom from Hidalgo; and (**b**) diatom from Jalisco. D: natural diatom; DC: diatom calcined with flux; DS: diatom calcined without flux.

Table 3. Properties of the studied diatoms.

Property	Sample from Hidalgo			Sample from Jalisco		
	Diatom Calcined with Flux	Diatom Calcined without Flux	Natural Diatom	Diatom Calcined with Flux	Diatom Calcined without Flux	Natural Diatom
Real density (g/cm^3)	2.37	2.22	2.15	2.35	2.20	2.13
Global density (g/cm^3)	0.50	0.52	0.61	0.52	0.54	0.62
Total porosity (%)	89.95	81.5	77.2	89.59	79.85	71.1
Specific surface (m^2/g)	16.391	17.74	22.53	16.59	17.94	22.07
Compressive strength (kg/cm^2)	17.7	16.49	15.00	18.3	17.51	17.00
Color	White	Rose	Cream-Grey	White	Rose	Cream-Grey
pH	10	7	7	10	8	7
Average pore size (µm)	7	3	1.5	6.7	4.6	1.8

4. Exchange of Metals

As can be seen in Table 4, diatoms show good efficiency for the cationic exchange of metals except for Cr^{6+}, where exchange corresponded to only 9%. This could be because Cr^{6+} in a reducing environment can be reduced from Cr^{6+} to Cr^{3+} to promote its elimination from solutions. However, when Cr^{6+} is present at high concentrations, it surpasses its capacity of reduction, which avoids its adequate elimination [24]. Consequently, all cations have similar concentrations and there is no reducing environment. Cr^{6+} could not be reduced to Cr^{3+}, demonstrating the low exchange efficiency of both diatoms for this cation. The similar efficiency values for other metals confirms the oxidizing environment present in solution. Accordingly, the diatomaceous material can be used favorably for treatment of residual waters both in the metallurgical industry and for municipal water. It can be seen that unlike polymerization processes where there is selectivity for the removal of cations, the diatoms studied here showed that this phenomenon does not occur because the pore walls resulting from calcination and the formation of potential sites for the adsorption of heavy metals allows the simultaneous removal of the cations in solution. These cations can be easily discharged with weak acid solutions, which enhances their reuse. For the case of As^{3+}, besides removal by cation exchange, the adsorption could play an important role. As^{3+} could be present in solution as $HAsO_4^{2-}$ at a pH of 8, and the removal could be due to the adsorption in some active alumina formed after the calcination process.

Table 4. Values of cationic exchange for metals using diatoms (pH = 8).

Metal	Initial Concentration in Solution (± 0.004 mg/L)	Final Concentration (in Solution) after Filtering with Diatom from Hidalgo (± 0.004 mg/L)	Final Concentration (in Solution) after Filtering with Diatom from Jalisco (± 0.004 mg/L)	Efficiency of Exchange of Diatom from Hidalgo (%)	Efficiency of Exchange of Diatom from Jalisco (%)
As^{3+}	5.27	0. 175	0.185	96.67	96.48
Ag^+	4.28	0.063	0.066	98.52	98.46.
Ni^{2+}	3.95	0.188	0.180	95.24	95.44
Cr^{6+}	4.09	3.790	3.710	7.33	9.29
Pb^{2+}	4.081	0.048	0.049	98.82	98.80

With respect to the exchange with arsenic using the studied diatoms, results show that once diatoms are saturated, a liberation of arsenic occurs (see Figure 8).
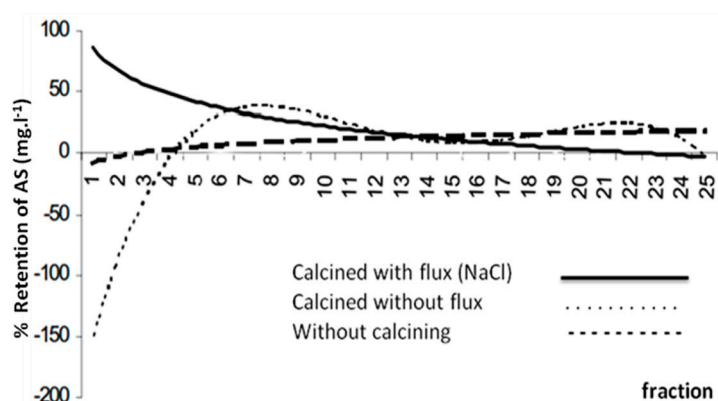

Figure 8. Arsenic exchange using diatoms.

5. Conclusions

According to the obtained chemical composition, it is concluded that diatoms are minerals incapable of effecting anionic exchange in a natural state. An adequate activation (calcination) can improve their anionic exchange capacity. Likewise, treating diatoms increased their efficiency in filtering processes, and they can be used in the absorption of cations due to their high retention

capacity. This increased with a heat treatment. For the retention of heavy metals, these diatoms showed good results, showing that the metals can be eliminated as long as they are not in very high concentration or in a too acidic solution. It can be also concluded that diatoms could be used in the treatment of wastewater contaminated with heavy metals. In the case of arsenic, it was observed that once the diatom was saturated with this element, its liberation to the solution occurred. For the case of Cr^{6+}, removal was not possible due to the absence of a reducing environment that can reduce Cr^{6+} to Cr^{3+} to allow its adequate removal.

Author Contributions: J. Hernández and E. Salinas conceived and designed the experiments; J. Hernández and M. I. Reyes performed and reviewed the experiments; E. Cerecedo, A. Arenas and V. Rodríguez made the XRD and SEM characterization of samples and helped in discussion. J. Hernández and A. D. Román performed the infrared analysis and interpreted the results. J. Hernández and E. Salinas wrote the paper. Finally, all author contributed in the revision and correction of observations form reviewers.

Conflicts of Interest: The authors declare no conflicts of interest.

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