

**SORPTION PROPERTIES OF MODIFIED  
CLINOPTILOLITE-AND MORDENITE-RICH  
TUFFS FOR MANGANESE REMOVAL  
FROM AQUEOUS SYSTEMS**

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### Abstract

Mexican clinoptilolite- and mordenite-rich tuffs were modified to obtain their sodium, iron, and silver forms in order to elucidate the effects of metallic species on the sorption properties of the natural zeolitic materials for the removal of  $\text{Mn}^{2+}$  from aqueous solutions. The interaction between the manganese solutions and the zeolitic materials was conducted by using a batch system. The unmodified and modified natural zeolites were characterized by scanning electron microscopy (SEM), X-ray diffraction, BET specific surface, and the points of zero charge. The amounts of Fe and Ag in both clinoptilolite- and mordenite-rich tuffs are similar ( $4.3 \pm 0.2$  %wt. and  $3.9 \pm 0.1$  %wt., respectively). The morphology and the crystalline structure of both materials demonstrate no change when Fe or Ag is added into the zeolitic network; however, the textural characteristics and the point of zero charge were affected by the presence of these metallic species with respect to unmodified zeolitic materials. The kinetic data were best fit by a pseudo-second order model, and the Freundlich model described the isotherms. The clinoptilolite- and mordenite-rich tuffs modified with silver removed manganese more efficiently than those modified with iron or sodium did. Therefore, both zeolitic materials could be used for the removal of manganese from aqueous solutions, independent of their structural characteristics.

### 1. Introduction

Human activities in achieving development have caused environmental pollution over the past few decades. Pollution by heavy metals is a topic of great social and environmental importance due to their toxicity and their ability to cause deterioration in water quality. Manganese can be found in natural waters in two forms, the reduced and soluble form ( $\text{Mn}^{2+}$ ) and the oxidized form ( $\text{MnO}_2$ ), pyrolusite. If the  $\text{Mn}^{2+}$  ions were not oxidized, these ions could easily escape through water treatment processes. Once in the distribution system, they could gradually be oxidized to insoluble manganese dioxide causing several problems, such as water discoloration, metallic taste, odor, turbidity, biofouling, corrosion and staining of laundry and plumbing fixtures (Roccaro et al. [30]).

Manganese is used in dry-cell batteries, glass, ceramics, fertilizer manufacturing, certain oxidizing agents (potassium permanganate ( $\text{KMnO}_4$ )), pesticides (Maneb or manganese ethylene-bisdithiocarbamate), and gasoline additives (MMT or methylcyclopentadienyl manganese tricarbonyl) (Garcia-Mendieta et al. [9]; Rajic et al. [29]). The most common health problems in workers exposed to high levels of manganese involve the nervous system. These health effects include behavioural changes and other nervous system effects, which include movements that may become slow and clumsy. When this combination of symptoms becomes sufficiently severe, it is referred to as “manganism” (irreversible Parkinson-like syndrome). The inhalation or ingestion of a large quantity of manganese may cause irritation to the lungs, which could lead to pneumonia. High concentrations of manganese can also cause problems in the respiratory tract and brain. Loss of sex drive and sperm damage has also been observed in men exposed to high levels of manganese (Beh et al. [1]; Inglezakis et al. [12]; and Lee et al. [16]).

The presence of manganese in natural and municipal water systems is of aesthetic, taste, and health concern. The World Health Organization has set a limit of 0.1mg/L for Mn(II) in drinking water (WHO [40]). Mexican legislation has set a limit of 0.15mg/L for manganese (NOM-127-SSA1-1994 [24]).

Various natural zeolites have been used as ion exchangers in the removal of ammonium ions from wastewater and drinking water, ionic cesium and strontium from radioactive wastes, and heavy metals in industrial wastewater (Kesraoui-Ouki et al. [15]; Leyva et al. [18]). The ion exchange property of the zeolites is due to the presence of the  $[\text{AlO}_4]^{5-}$  tetrahedra in its structure and the deficiency of the charge is compensated by a cationic species. Therefore, unmodified natural zeolites have no ability to exchange anions. Modified zeolites are an alternative adsorbent for non-ionizable organic compounds, as well as anions. It has been shown that the cation exchange capacity of natural zeolites is dependent on the type, origin and treatment of zeolite material. One of

the most important features provided by the different species of zeolites for environmental protection is the number of cations available for ion exchange (Semmens [31]). The cation exchange capacity of the zeolites can be modified according to the cation exchange used in the ion exchange treatment (Loizidou and Townsend [19]).

The aim of this work was to modify a clinoptilolite-rich tuff from Villa de Reyes (San Luis Potosí) and a mordenite-rich tuff from Cruillas (Tamaulipas) to obtain their sodium, iron, and silver forms and to determine the effect of the metallic species ( $\text{Na}^+$ ,  $\text{Fe}^{3+}$ , and  $\text{Ag}^+$ ) on the sorption properties of the natural zeolitic materials for the removal of manganese ( $\text{Mn}^{2+}$ ) from aqueous solutions, with consideration given to the kinetics and isotherms of the sorption processes. This research is important due to  $\text{Ag}^+$  and  $\text{Fe}^{3+}$  has bactericide properties and these systems could be used simultaneously for the water disinfection and  $\text{Mn}^{2+}$  removal from aqueous media. In the present work, only the sorption properties will be discussed.

## 2. Experimental

### 2.1. Materials

A clinoptilolite-rich tuff (CLD) from Villa de Reyes (San Luis Potosí, México) and a mordenite-rich tuff (MOR) from Cruillas (Tamaulipas, México) were used in this work. The materials were ground in an agate mortar and sieved. The mesh size chosen in the present work was 30-mesh.

### 2.2. Treatment of zeolite-rich tuffs

#### 2.2.1. Modification with Na

To improve the ion exchange of the zeolitic materials (Díaz-Nava et al. [4]) to obtain Fe- or Ag-modified clinoptilolite- or mordenite-rich tuffs with different characteristics, 300g of the raw zeolitic materials were

treated with 600mL of 0.1M NaCl solution under reflux for 5h. The phases were separated and this process was repeated once more while changing the NaCl solution. The phases were separated by centrifugation, and the solid phases were washed with deionized water until  $\text{Cl}^-$  was eliminated by using the  $\text{AgNO}_3$  test. Then, the zeolitic samples were dried at  $80^\circ\text{C}$  for 24h. These samples were called CLINa and MORNa.

### **2.2.2. Treatment with Fe or Ag**

CLINa or MORNa (100g) were treated with 200mL of 0.1M  $\text{FeCl}_3$  solution under reflux for 5h. This process was repeated once after changing the solution. The solid phase was separated by centrifugation and was washed with deionized water until  $\text{Cl}^-$  was eliminated using the  $\text{AgNO}_3$  test and then dried at  $80^\circ\text{C}$  for 24h. The samples were named CLIFe and 110 MORFe. The procedure mentioned above was repeated with a 0.1M  $\text{AgNO}_3$  solution. The zeolitic material in this case was washed with deionized water until the excess of  $\text{Ag}^+$  was eliminated by using the NaCl test. The resultant zeolitic materials were named CLIaAg and MORaAg.

## **2.3. Characterization techniques**

### **2.3.1. Morphology and elemental composition**

For scanning electron microscopy observations, the samples were mounted directly onto the sample holders. The images were collected at 15kV using a double beam FEI Nova 200 Nanolab electron microscope, and the chemical composition was determined with an OXFORD electron dispersive spectroscopy (EDS) system coupled with a JEOLJSM 5900 electron microscope. Three tests were performed for each unmodified zeolitic material (CLI and MOR), as well as for sodium-, iron- and silver-modified natural zeolites (CLINa, MORNa, CLIFe, MORFe, CLIaAg, and MORaAg, respectively).

### 2.3.2. X-ray diffraction

X-ray diffraction (XRD) analysis was performed on the zeolitic materials (treated and untreated) to confirm the crystal structure and the identity of the components of the zeolitic material. Powder diffractograms of the samples were obtained with a Siemens D500 diffractometer coupled with a copper-anode X-ray tube. Conventional diffractograms were used to identify the compounds present in the zeolitic rocks.

### 2.3.3. Textural properties

Specific area measurements were obtained via a BELSORP MAX analyzer by using  $N_2$ . Before the analysis, zeolitic samples (approximately 10mg) were degassed for approximately 24h at 250°C. The surface area was determined by using the BET multipoint method, and the sorption isotherms were analyzed at relative pressures between 0.001 and 1. The pore volume, size and type were obtained, in addition to the surface area.

### 2.3.4. Point of zero charge

The value of the  $pH_{pzc}$  of each material was determined by using the modified pH drift method (Faria et al. [8]; Zaini et al. [41]; Ma et al. [21]; and Jiménez-Cedillo et al. [14]): 0.15g of CLI, CLINa, CLIFe, CLIaG, MOR, MORNa, MORFe, and MORAg were mixed with 50mL of 0.01M NaCl at different initial pH values. The initial pH of the solution was adjusted between 2 and 12 by adding 0.1M HCl or 0.1M NaOH solution. The suspensions were allowed to equilibrate for 24h under agitation at 25°C, and the final pH values were measured by using the pH STAT Controller (Meter Lab PHM 290). The pH at the point of zero charge,  $pH_{pzc}$ , corresponds to the pH at which the curve crosses the straight-line that fits the points  $pH_{initial} = pH_{final}$ .

## 2.4. Mn(II) sorption

### 2.4.1. Kinetics

A batch system was employed to determine the manganese sorption kinetics for CLINa, CLIFe, CLIAg, MORNa, MORFe, and MORAg. Using rotary agitation, 150mg of the modified materials was mixed with 15mL of a 4mg/L  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  solution (pH 6) at room temperature (18°C) for 5, 10, 15, 20, and 30min and 1, 2, 3, 5, and 24h using Glas-Col equipment. Duplicates of each experiment were performed. The materials were separated by centrifugation at 80rpm for 5min using a BHG 1100 centrifuge. The manganese was analyzed in the aqueous phase, using a GBC 932 Plus atomic absorption spectrometer with an air-acetylene flame and a hollow cathode lamp at 280.1nm. The amount of Mn(II) per gram of the sorbent's  $q_e$  (mg/g) was calculated using the following equation:

$$q_e = [(C_o - C_e) \times V]/w, \quad (1)$$

where  $C_o$  and  $C_e$  are the initial and final Mn concentration (mg/L) in the solution, respectively,  $V$  is the volume of the solution (L), and  $w$  is the mass of the adsorbent (g).

### 2.4.2. Isotherms

The adsorption experiments were conducted as follows: 150mg of modified materials were put in contact with 15mL of 2.5, 5, 7.5, 10, 25, 50, 75, 100, 150, 200, 250, and 300mg/L Mn solutions at pH 6.0. The mixtures were shaken for 24h at room temperature (18°C). Each experiment was performed in duplicate. The zeolitic materials were separated via centrifugation. The manganese was measured at a wavelength of 280.1nm using a GBC 932 Plus atomic absorption spectrometer.

### 3. Results and Discussion

#### 3.1. Characterization

##### 3.1.1. Elemental composition

The principal components of CLI are O, Mg, Al, Si, K, Ca, and Fe (Table 1), and the principal components of MOR are O, Na, Mg, Al, Si, K, Ca, and Fe. It is reasonable to consider that Na, Mg, K, and Ca are the extra framework cations that compensate for the deficiency of charge in the zeolite network (Breck [2]; Tsitsishvili et al. [37]). According to the concentration of Na, Mg, K, and Ca in CLI (Table 1), it is considered to be a potassium zeolite type and the mordenite is a sodium-calcium zeolite type. Similar elemental composition was obtained for clinoptilolite of Chihuahua, México (Jiménez-Cedillo et al. [13]).

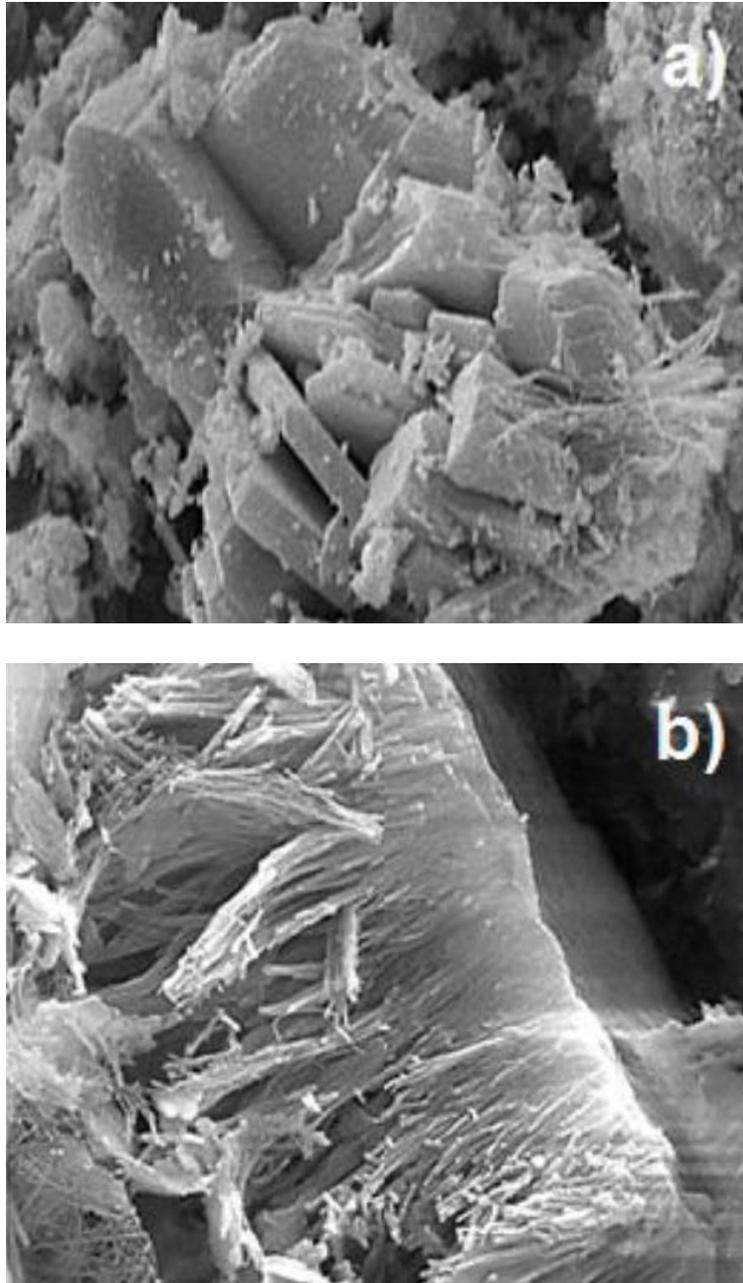
**Table 1.** Elemental composition of unmodified and modified zeolitic materials

Elmt.	Composition (wt. %)							
	CLI	CLINa	CLIFe	CLIAg	MOR	MORNa	MORFe	MORAg
O	52.7 ± 1.2	52.9 ± 0.1	42.9 ± 9.7	56.7 ± 1.4	56.5 ± 2	55.6 ± 0.6	56.7 ± 1.2	55.8 ± 0.2
Na	ND	0.7 ± 0.1	ND	ND	1.5 ± 0.2	1.6 ± 0.1	1.1 ± 0.1	0.7 ± 0.06
Mg	0.3 ± 0.01	0.3 ± 0.01	ND	ND	0.5 ± 0.2	0.3 ± 0.03	0.84 ± 0.1	1 ± 0.4
Al	3.8 ± 0.05	3.2 ± 0.3	6.4 ± 0.2	5.5 ± 0.2	4.2 ± 0.3	3.6 ± 0.2	4.9 ± 0.1	5 ± 0.1
Si	17.1 ± 0.6	14.6 ± 2.9	38 ± 4.9	25.1 ± 1.2	21.8 ± 1.3	25.2 ± 1.3	26.3 ± 1.5	30.5 ± 0.9
K	2.1 ± 0.2	1.5 ± 0.06	6.4 ± 3.4	2.7 ± 0.08	0.3 ± 0.02	0.3 ± 0.06	0.39	0.6 ± 0.1
Ca	0.7 ± 0.1	0.5 ± 0.1	2.3 ± 1.5	0.8 ± 0.06	1.3 ± 0.2	1.3 ± 0.01	1.4 ± 0.04	1.5 ± 0.2
Ag	ND	ND	ND	3.9 ± 0.4	ND	ND	ND	4.4 ± 0.7
Fe	0.7 ± 0.1	0.5 ± 0.04	4.3 ± 0.4	0.6 ± 0.1	1.2 ± 0.8	0.5 ± 0.02	4.6 ± 1.1	1 ± 0.4

After treatment with a NaCl solution, the Na concentration in CLINa increases from 0 to  $0.7 \pm 0.1\%$ ; however, this is not found in MORNa (before NaCl:  $1.5 \pm 0.2$  wt.%, after NaCl:  $1.6 \pm 0.1$  wt.%). A similar result has been observed by other researchers (Diaz-Nava et al. [4]; Jiménez-Cedillo et al. [13]). In the zeolite-rich tuffs treated with  $\text{FeCl}_3$  and  $\text{AgNO}_3$  solutions, the sodium concentration diminishes more significantly for CLIFe and CLIAg than for MORFe and MORAg (Table 1). The amount of Fe and Ag are similar in both modified natural zeolites (CLIFe  $4.3 \pm 0.4$  %wt. and MORFe  $4.6 \pm 1.1$  %wt.; CLIAg  $3.9 \pm 0.4$  %wt. and MORAg  $4.4 \pm 0.7$  %wt.). Therefore, these results suggest that the  $\text{Na}^+$  ions play an important role in the conditioned processes of the zeolite-rich tuffs with the iron and silver salts, due to an ion exchange mechanism. It also indicates that the zeolite-rich tuffs are more selective for iron than for silver, considering the meq exchanged for both ionic species (2.38meq Fe(III)/g and 0.38meq Ag(I)/g). It is important to mention that the initial  $\text{FeCl}_3$  solutions were in the range of pH 2 to 3. For this reason, it is also thought that  $\text{H}^+$  could compete for the ion exchange sites in the zeolite network (Olguin et al. [25]).

### 3.1.2. Morphology

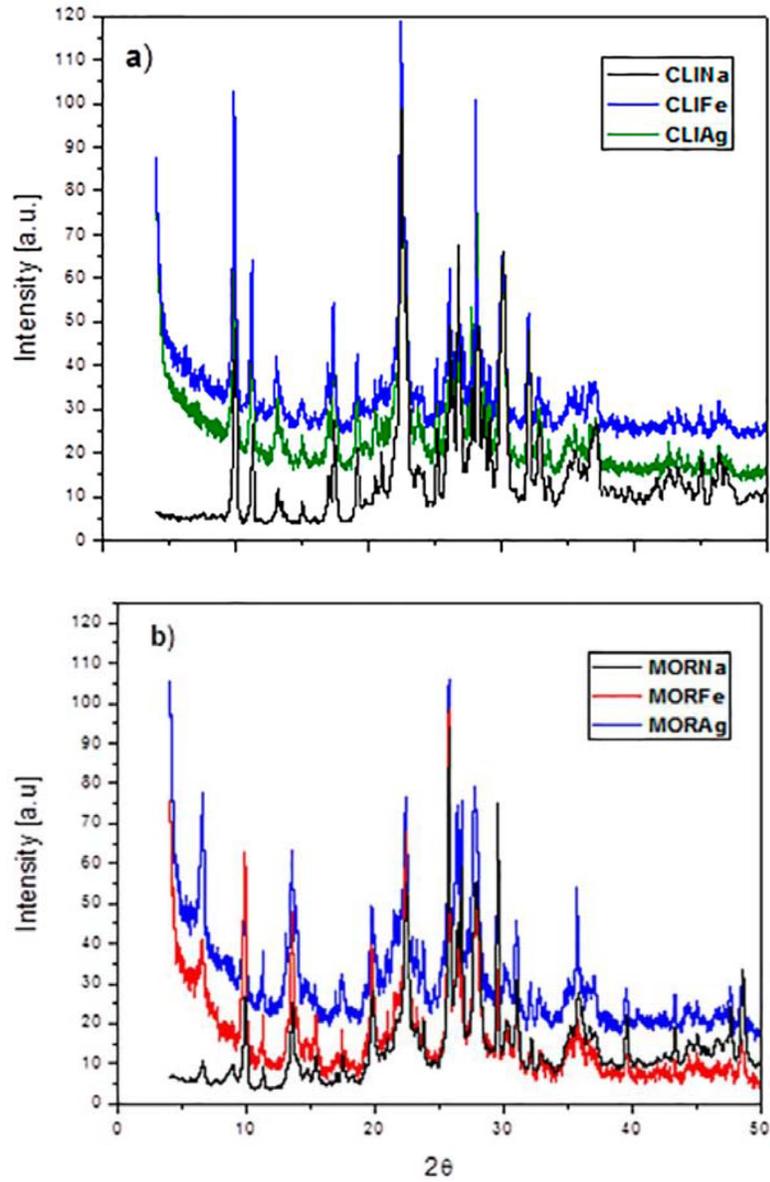
The SEM images of CLI show typical morphologies of clinoptilolite, which occur as euhedral plates and laths (Figure 1(a)). Most crystals display characteristic monoclinic symmetry and many are coffin-shaped (Mumpton and Clayto [23]). No changes are observed in the morphology of the clinoptilolite crystals of CLI after its treatment with NaCl, AgCl or  $\text{FeCl}_3$  solutions. Mordenite is also a component of CLI. MOR shows morphologies, which occur as thin fibers crystals displaying orthorhombic symmetry (Figure 1(b)). No changes are observed in the morphology after the different treatments.



**Figure 1.** SEM images of (a) clinoptilolite-rich tuff from San Luis Potosí; and (b) mordenite-rich tuff from Tamaulipas, Mexico.

### 3.1.3. Mineral composition and crystallinity

The JCPDS cards for clinoptilolite (25-1349) and for mordenite (29-1257) confirm the presence of these mineral components in the zeolitic rocks from Villa de Reyes (San Luis Potosí, México) and Cruillas (Tamaulipas, México), respectively. The X-ray diffraction patterns of the sodium forms of clinoptilolite and mordenite-rich tuffs are compared with those of the iron and silver forms of both natural zeolites: while the intensity of the reflections varies, the position of the reflections does not (Figure 2). Similar results were observed for CLI of San Luis Potosí modified with HDTMA (Torres-Pérez et al. [36]), for Romanian zeolite supported with silver (Orha et al. [26]) and natural zeolites modified with iron and iron-manganese (Jiménez-Cedillo et al. [13]). These results suggest the presence of  $\text{Fe}^{3+}$  and  $\text{Ag}^+$  in the ion exchange sites of the zeolitic network, which are most likely M1 and M2 in clinoptilolite (Concepción-Rosabal et al. [3]) and A, C, D, or E in mordenite (Sun et al. [33]).



**Figure 2.** The XRD pattern of a) CLI and b) MOR in comparison with the different modified materials.

#### 3.1.4. Textural characteristics

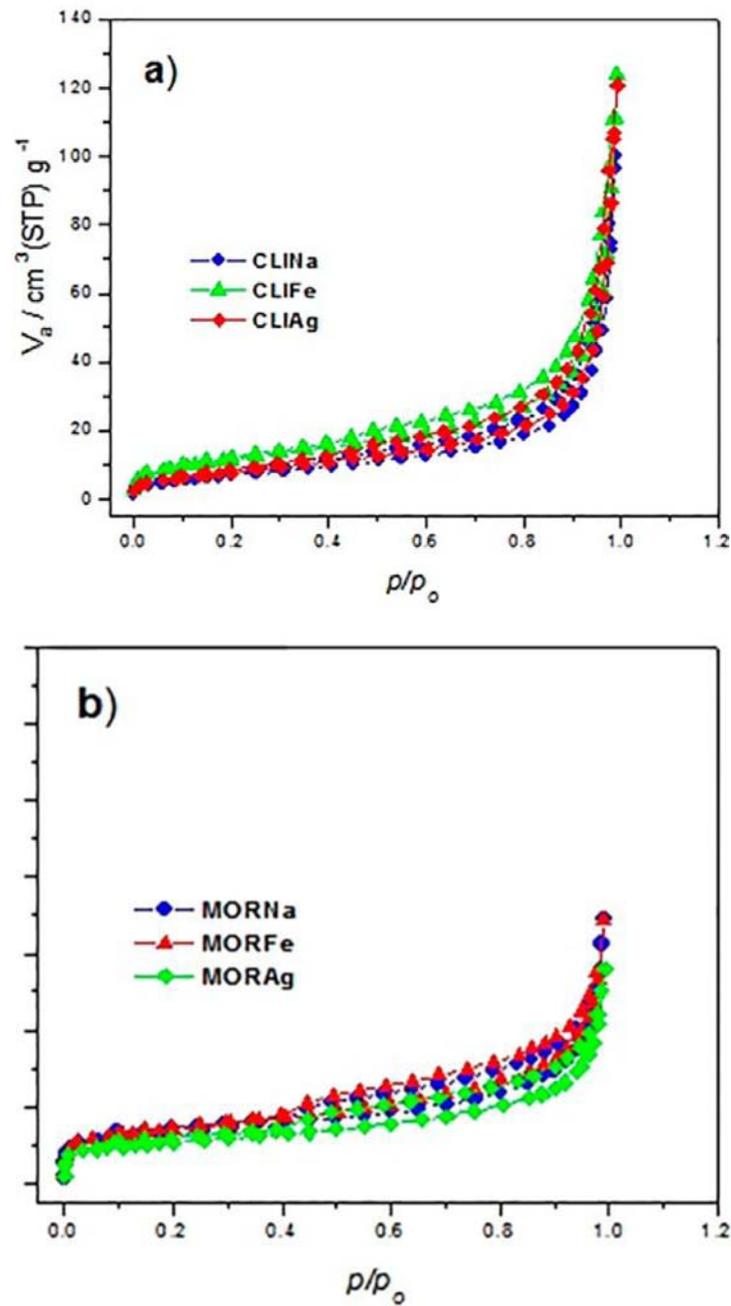
The specific surface area of CLI is 3.9 times smaller than that of MOR, which could be due to the composition of each zeolitic rock and the structural characteristics of each zeolite. After the zeolitic materials were treated with the NaCl solution to obtain CLINa and MORNa, the specific surface area varied with respect to that of the untreated samples (Table 2). This variation was more notable for MORNa than for CLINa. The specific surface area was 2.3 times higher for MOR than for MORNa. The specific surface area increased 1.52 and 1.15 times for CLIFe and CLIaG with respect to CLINa. When MORNa was modified with Fe and Ag, a slight increase in the specific surface area of 1.1 times was observed in MORFe and it diminishes in 1.19 times for MORAg relative to MORNa. In previous works, it has been reported that the specific surface area increases in iron-modified zeolitic materials due to (a) the non-crystalline Fe formations located in the cationic positions of the zeolite channels, (b) binuclear and oligonuclear Fe complexes in extra-framework positions, and (c) amorphous iron oxides of FeOx type located at the surface of the zeolite crystal (Pérez-Ramírez et al. [28]; Doula [6]).

For CLI modified with Fe and Ag, the monolayer volume and the total pore volume are higher than that for CLINa (Table 2). In the case of MOR modified with Fe, the monolayer volume and the total pore volume are higher than that for MORNa, but these parameters are lower for MORAg than those found for MORNa (Table 2). It is important to mention that CLIFe and MORFe, as well as CLIaG and MORAg, have similar specific surface area (38.3 and 41m<sup>2</sup>/g; 29 and 30.9m<sup>2</sup>/g, respectively). These results confirm that Fe<sup>3+</sup> and Ag<sup>+</sup> in the natural zeolite modified the textural parameters of these zeolitic materials with respect to their sodium forms. Similar results were found for an iron-modified clinoptilolite from Northern Greece (Doula [5]). Therefore, it is expected that the textural characteristics of CLIFe, CLIaG, MORFe, and MORAg play a role in Mn(II) adsorption from aqueous media.

**Table 2.** Textural characteristics of unmodified and modified clinoptilolite- and mordenite-rich tuffs

Sample	Specific area (BET) ( $\text{m}^2/\text{g}$ )	Monolayer volume $V_m$ ( $\text{cm}^3/\text{g}$ )	Total pore volume $V_p$ ( $\text{cm}^3/\text{g}$ )
CLI	21.65	4.9751	0.1286
CLINa	25.21	5.7923	0.1542
CLIFe	38.39	8.821	0.1839
CLIAg	29.08	6.6801	0.1774
MOR	85.1	19.533	0.1231
MORNa	36.87	8.4713	0.1033
MORFe	41.04	9.4281	0.1046
MORAg	30.91	7.1021	0.0828

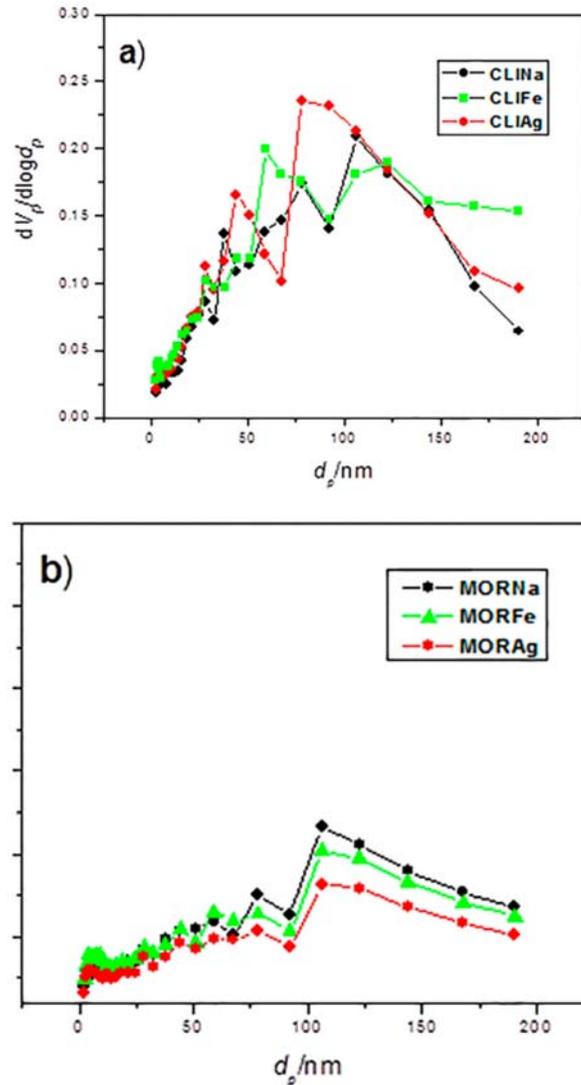
According with the IUPAC classification of  $\text{N}_2$  adsorption-desorption isotherms, those found by clinoptilolite- and mordenite-rich tuffs were classified as type IV (Figure 3), characteristic by their hysteresis loop which is associated with capillary condensation taking place in mesopores, and the limiting uptake over a range of high  $p/p_0$  (Sing [32]). The initial part of the Type IV isotherm is attributed to monolayer multilayer adsorption since it follows the same path as the corresponding part of a Type II isotherm obtained with the given adsorptive on the same surface area of the adsorbent in a non-porous form. Type IV isotherms are given by many mesoporous adsorbents (Wang et al. [39]).



**Figure 3.** Nitrogen adsorption-desorption isotherms for (a) modified clinoptilolite-rich tuffs and (b) modified mordenite-rich tuffs.

The type of hysteresis loop founded in this work was H3. This loop, which does not exhibit any limiting adsorption at high  $p/p_0$ , is characteristic of aggregates of particles forming pores with non-uniform sizes and shapes. The width of hysteresis between adsorption- desorption branch is small in all modified forms of clinoptilolite-rich tuff, indicating that the materials exhibit a homogeneous porosity, which is characteristic of zeolites (Leofanti et al. [17]). In modified mordenite-rich tuffs, the hysteresis width between adsorption- desorption branch of intermediate relative pressures drops abruptly, indicating a disordered domain that may result from the collapse of the structures, therefore the modified forms of mordenite exhibit heterogeneous porosity.

The modified clinoptilolite-and mordenite-rich tuffs present a pore size between 25 and 150nm and the distribution depends on the ion, which modified the zeolitic network ( $\text{Na}^+$ ,  $\text{Fe}^{3+}$  or  $\text{Ag}^+$ ). It is important to mention that the pore diameter depends of the structural characteristics of each zeolitic material as was expected (CLI and MOR), Figure 4.

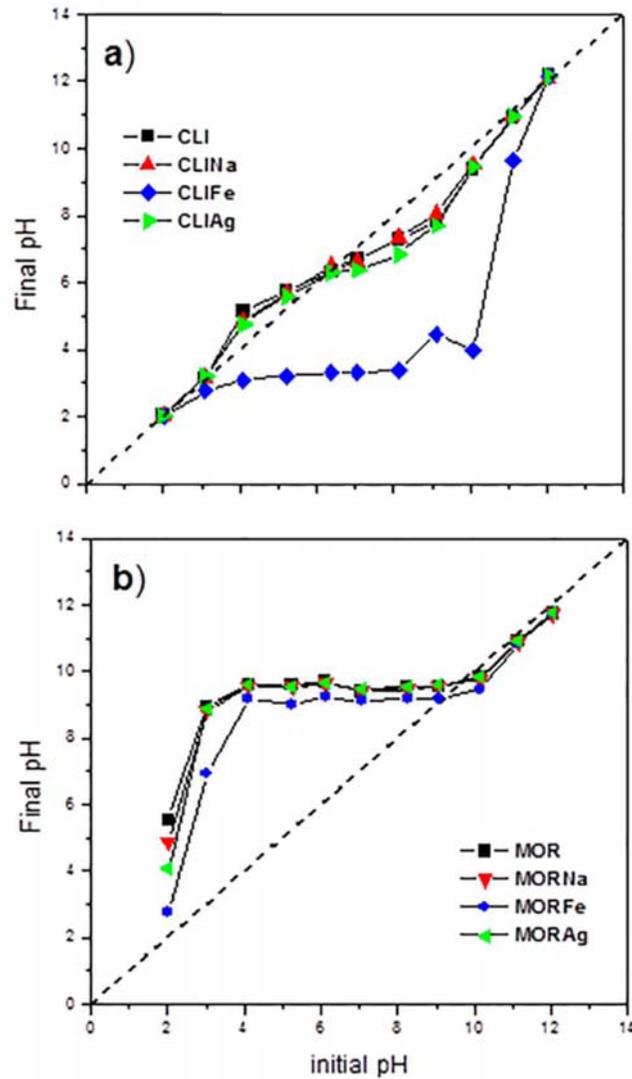


**Figure 4.** Pore size distribution of modified zeolitic materials (a) CLI and (b) MOR.

### 3.1.5. Point of zero charge

An important indicator of the net surface charge from each sorbent material is  $pH_{pzc}$ . The interaction of the cationic and anionic species in solution with the surface of the zeolitic materials depends on this value.

It was found that CLI materials have lower  $\text{pH}_{\text{pzc}}$  values than MOR materials, independent of the cation ( $\text{Fe}^{3+}$  or  $\text{Ag}^+$ ) that modified the zeolitic network (Figure 5).



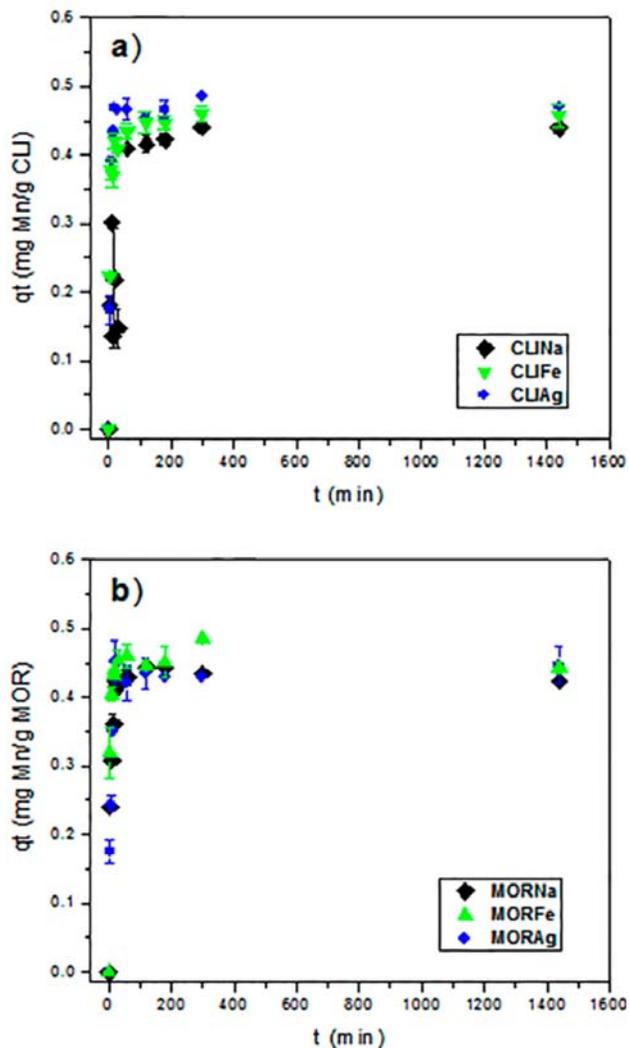
**Figure 5.**  $\text{pH}_{\text{pzc}}$  for unmodified and modified clinoptilolite- and mordenite-rich tuffs.

The pH at the point of zero charge,  $\text{pH}_{\text{pzc}}$ , is the pH at which the curve crosses the straight line that fits the points  $\text{pH}_{\text{Initial}} = \text{pH}_{\text{Final}}$  (Lopez-Ramon et al. [20]), as was mentioned in the corresponding experimental section. The clinoptilolite-rich tuffs (CLI, CLINa, CLIFe, and CLIaG) present an acidic surface; meanwhile, the mordenite-rich tuffs (MOR, MORNa, MORFe, MORaG) present a basic surface. CLIFe, CLIaG, MORFe, and MORaG have a  $\text{pH}_{\text{pzc}}$  of 2.1, 6.0, 9.24, and 9.68, respectively. When the pH is lower than these values, the material has positively charged sites and sorbs anions; when the pH is higher, the surface has negatively charged sites and predominantly sorbs cations. This point is an important consideration in decontamination processes of polluted water.

### 3.2. Mn(II) sorption

#### 3.2.1. Kinetics

It was found that Mn(II) was adsorbed by all zeolitic materials during the first minutes of contact time until equilibrium was reached at 60, 20, and 15 min for CLINa, CLIFe, and CLIaG, respectively. In the case of MORNa, the equilibrium was reached at 20min, whereas for MORFe and MORaG it was reached at 30 min. It is important to note that the cation that modified the zeolitic material ( $\text{Na}^+$ ,  $\text{Fe}^{3+}$  or  $\text{Ag}^+$ ) influences the time for Mn(II) to reach the sorption equilibrium ( $t_e$ ) and it follows the order:  $t_{e\text{MnCLINa}} > t_{e\text{MnMORFe}} = t_{e\text{MnMORaG}} > t_{e\text{MnCLIFe}} = t_{e\text{MnMORNa}} > t_{e\text{MnCLIaG}}$ . The amount of Mn(II) adsorbed by the zeolitic materials was approximately 0.45mg/g (Figure 6). In all cases, an initially fast sorption of Mn(II) was observed, which could be attributed to a greater concentration gradient and more available sorption sites. In the second step, the sorption was slower once the equilibrium was reached. This behaviour is similar to that reported for the sorption of  $\text{Mn}^{2+}$  by green tomato husk (García-Mendieta et al. [10]), coal (Pereira et al. [27]), zeolite-rich tuffs from Serbia (Rajic et al. [29]), sugarcane bagasse, activated carbon (Esfandiar et al. [7]), and *Ulva* sp. biomass (Vijayaraghavan and Joshi [38]).



**Figure 6.** Manganese sorption by unmodified and modified (a) clinoptilolite and (b) mordenite as a function of time.

### 3.2.1.1. Pseudo-first order kinetic model

The experimental data (Figure 6) were fit to different kinetic models to obtain the parameters that describe the Mn(II) sorption processes by applying a non-linear regression analysis with the ORIGIN 8.0 program for Windows.

The pseudo-first order equation of Lagergren is generally expressed as follows:

$$q_t = q_e(1 - \exp(-K_L t)), \quad (2)$$

where  $q_t$  (mg/g) is the amount of Mn(II) sorbed at time  $t$ ,  $q_e$  (mg/g) is the amount of Mn(II) sorbed at equilibrium and  $K_L$  ( $\text{min}^{-1}$ ) is the Lagergren rate constant.

Table 3 shows the pseudo-first order model parameters that correspond to Mn(II) sorption by modified zeolitic materials. The amount of Mn(II) sorbed at equilibrium ( $q_e$ ) was similar in all cases, independent of the characteristics of the crystalline networks (clinoptilolite or mordenite) or the cations ( $\text{Na}^+$ ,  $\text{Fe}^{3+}$  or  $\text{Ag}^+$ ) that modified the zeolitic materials. However, the Lagergren rate constant ( $k_L$ ) varies as follows:  $k_{LMnMORFe} > k_{LMnCLIFe} > k_{LMnCLIAg} = k_{LMnMORNa} > k_{LMnMORA} > k_{LMnCLINa}$ . It is clear that the Lagergren rate constant depends on the nature of zeolitic materials as well as the chemical nature of the metallic species that occupy the ion exchange sites in the natural zeolites.

**Table 3.** Kinetic parameters obtained from the sorption of Mn(II) by modified zeolitic materials

Sample	$q_e$ , exp. Mg/g	Pseudo-first-order			Pseudo-second-order		
		$q_e$ mg/g	$K_L$ $\text{min}^{-1}$	$r^2$	$q_e$ mf/g	$k_2$ g/mg min	$r^2$
CLINa	0.44	0.43	0.037	0.86	0.45	0.13	0.88
CLIFe	0.46	0.44	0.15	0.99	0.47	0.57	0.99
CLIAg	0.47	0.47	0.14	0.99	0.50	0.49	0.96
MORNa	0.42	0.43	0.14	0.99	0.45	0.58	0.99
MORFe	0.44	0.45	0.23	0.99	0.47	1.13	0.99
MORA	0.45	0.44	0.11	0.98	0.46	0.39	0.96

$q_e$  exp. is the amount of Mn(II) sorbed by the zeolitic materials as a result of the experiment.

### 3.2.1.2. Pseudo-second order kinetic model

The pseudo-second order kinetic model developed by Ho and McKay [11] is based on experimental information about solid phase sorption. In general, it has been applied to heterogeneous systems, where the sorption mechanism is attributed to chemical sorption.

The pseudo-second order equation is generally expressed as

$$t/q_t = (1/k_2q_e^2) + (t/q_e), \quad (3)$$

where  $(g/mg \text{ min})$  is the rate constant of the pseudo-second order reaction,  $q_t$  (mg/g) is the amount of Mn(II) sorbed at time  $t$ , and  $q_e$  (mg/g) is the amount of Mn(II) sorbed at equilibrium. The pseudo-second-order model assumes that chemisorption is the rate-limiting step, which involves valence forces from the sharing or exchange of electrons between the sorbent and the sorbate. Although the experimental data can be fit to a pseudo-first-order kinetic model, the experimental data also fit well to the pseudo-second order kinetic model (Table 3), based on the determination coefficients ( $r^2$ ). Due to the characteristics of the natural zeolites, which were considered as heterogeneous systems, the latter model provides a better description of the kinetic behaviour of Mn(II) sorption in these materials. The  $q_e$  values were approximately the same in all zeolitic materials. This result was similar to when the pseudo-first order kinetic model was applied (Table 3). The  $k_2$  parameter of the materials, which corresponds to the rate constant of the pseudo-second order model, were in the following order:

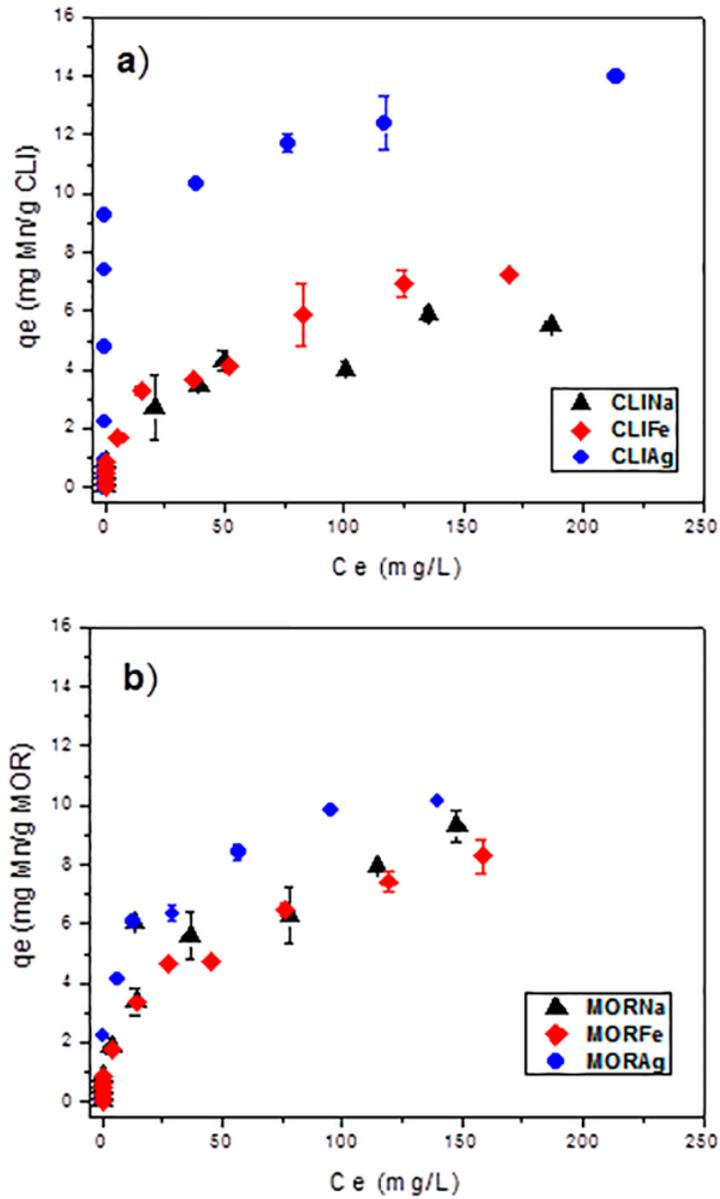
$k_{2\text{MnMORFe}} > k_{2\text{MnMORNa}} > k_{2\text{MnCLIFe}} > k_{2\text{MnCLIAg}} > k_{2\text{MnMORAg}} > k_{2\text{MnCLINa}}$ .  
 These results confirm that the pseudo-second order rate constant depends on the structural characteristics of the zeolitic materials and the cations to be exchanged for  $\text{Mn}^{2+}$  in aqueous media.

Other investigations have also reported that the sorption of Mn(II) by *Ulva* sp. biomass (Vijayaraghavan et al. [38]), PONP biomass (Ma et al. [22]), activated Ch-zeolite (Taffarel and Rubio [34]), and Mexican clinoptilolite-rich tuffs (García-Mendieta et al. [9]) are well described by the pseudo second-order kinetic model, which considers chemi-adsorption to be the rate controlling step.

### 3.2.2. Isotherms

Figure 7 depicts the sorption isotherms for Mn(II) using CLINa, CLIFe, CLIaG, MORNa, MORFe, and MORaG. The maximum sorption of Mn(II) by the modified clinoptilolite-rich tuffs differs depending on the cations in the zeolite network, and it was found to be 5.49, 7.24, and 14.02mg/g for CLINa, CLIFe, and CLIaG, respectively. This behaviour was slightly different in the case of the sorption of Mn(II) by modified mordenite-rich tuffs, which was determined to be 9.33, 10.14, and 8.29 mg/g for MORNa, MORFe, and MORaG, respectively.

The purpose of the adsorption isotherms is to relate the adsorbate concentration in the bulk to the adsorbed amount at the interface. The Langmuir and Freundlich isotherms are most commonly used to describe the adsorption behaviour and, for this reason, were considered in the present work.



**Figure 7.** Mn(II) sorption isotherms by unmodified and modified (a) clinoptilolite and (b) mordenite.

### 3.2.2.1. Langmuir isotherm

The Langmuir isotherm assumes that monolayer sorption occurs on a homogeneous surface without interaction between the sorbed molecules. It is described as follows:

$$q_e = Q_o K_L C_e / 1 + K_L C_e, \quad (4)$$

where  $q_e$  is the sorption of sorbate to the sorbent (mg/g),  $C_e$  is the sorbate concentration (mg/L),  $Q_o$  is the maximum capacity of the sorbent (mg/g), and  $K_L$  is a parameter that is related to the sorption energy (L/mg).

The Langmuir model was used to evaluate the interaction energy and the maximum capacity of each zeolitic material for Mn(II) sorption. The theoretically calculated  $Q_o$  values obtained using the Langmuir model show that CLIAg and MORAg sorb the major amount of Mn(II) from aqueous solution followed by MORFe and CLIFe (Table 4). These results suggest that the zeolitic materials modified with Ag are more selective for Mn(II) than those modified with iron, which are more selective than those modified with sodium. The  $K_L$  parameter is higher for Mn(II) sorbed by MORAg than by CLIAg, which indicates that the adsorption energy will play an important role in the desorption processes to regenerate the zeolitic materials.

Therefore, the textural properties of CLIAg and MORAg (Table 2), the manganese chemical species in solution and the  $\text{pH}_{\text{pzc}}$  (Figure 5) are important factors in the sorption processes.

**Table 4.** Langmuir and Freundlich parameters obtained from the Mn(II) isotherms for clinoptilolite- and mordenite-rich tuffs

Sample	Langmuir		$r^2$	Freundlich		
	$Q_o$ mg/g	$K_L$ L/mg		$K_F$ (mg/g)(L/mg) <sup>1/n</sup>	$1/n$	$r^2$
CLINa	6.37	0.034	0.97	1.14	0.3095	0.97
CLIFe	8.66	0.026	0.98	0.95	0.4016	0.99
CLIAg	14.74	0.056	0.71	5.41	0.1798	0.71
MORNa	8.89	0.069	0.96	1.75	0.3236	0.97
MORFe	9.22	0.035	0.99	1.12	0.3984	0.99
MORAg	10.53	0.087	0.98	1.85	0.3610	0.97

**3.2.2.2. Freundlich isotherm**

The Freundlich isotherm is widely used to describe sorption on a surface with a heterogeneous energy distribution. It is described as follows:

$$Q_e = K_F C_e^{1/n}, \quad (5)$$

where  $q_e$  (mg/g) and  $C_e$  (mg/L) are the concentrations of the sorbate in the solid and liquid phases, respectively.  $K_F$  is the equilibrium constant describing the sorption capacity (mg/g) (L/mg)<sup>1/n</sup>, where  $n$  is the affinity constant that describes sorption intensity ( $1/n$ ).

From the Freundlich model, the CLIAg had the largest  $K_F$  value, which was 2.9 times greater than that for MORAg. The values of  $1/n$  were  $< 1$  in all cases for the sorption of Mn(II) in the modified zeolitic materials, indicating favorable sorption at low concentrations (Table 4).

In general, the experimental data obtained from the isotherms of Mn(II) by the zeolitic materials were well fit for both the Langmuir and Freundlich models according to the determination coefficients ( $r^2$ ) (Table 4). However, the Langmuir equation assumes that the surface is homogeneous and contains a single sorption layer. The natural materials

used in this work are heterogeneous adsorbents because of their composition. Therefore, the Freundlich model is the most appropriate to describe the processes by which Mn(II) is adsorbed on the modified zeolite-rich tuffs.

For comparison purposes, the maximum capacities of  $\text{Mn}^{2+}$  from various zeolitic materials are presented in Table 5 along with the results obtained in this work. The zeolitic materials used in this work have similar adsorption capacity in comparison to clinoptilolite-rich tuffs from Tehuacán, Puebla (Mexico) (García-Mendieta et al. [9]) and zeolite-rich tuffs from Vranjska Banja (Serbia) (Rajic et al. [29]).

**Table 5.** Maximum adsorption capacities of zeolitic materials for Mn(II)

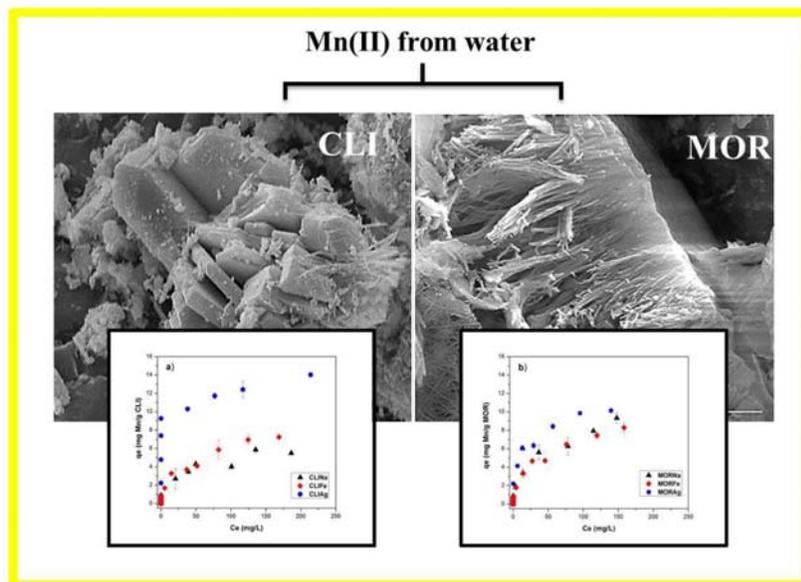
Zeolitic materials	Maximum Mn(II)	
	adsorption capacity, $Q_o$ (mg/g)	Reference
Clinoptilolite–iron oxide system	27.1	[29]
Modified Ch-zeolite with:		[38]
NaCl	21.1	
NaOH	20.8	
$\text{Na}_2\text{CO}_3$	19.7	
$\text{NH}_4\text{Cl}$	18.4	
Zeolite-rich tuff from the Vranjska Banja deposit (Serbia)	10.0	[3]
Mexican clinoptilolite-rich tuff	6.3	[2]
Manganese oxide coated zeolite	30.8	[41]
Sodium clinoptilolite-rich tuff	6.3	Present work
Iron clinoptilolite-rich tuff	8.6	Present work
Silver clinoptilolite-rich tuff	14.7	Present work
Sodium mordenite-rich tuff	8.8	Present work
Iron mordenite-rich tuff	9.2	Present work
Silver mordenite-rich tuff	10.5	Present work

#### 4. Conclusion

Clinoptilolite is the main component of the zeolite-rich tuff from Villa de Reyes (San Luis Potosí, México), and mordenite is the main component in the zeolite-rich tuff from Cruillas (Tamaulipas, México). The treatment of the zeolite-rich tuffs with sodium chloride, ferric chloride, and silver chloride solutions does not modify the morphology and structure of the zeolitic materials. The content of silver and iron is similar in both zeolite-rich tuffs. The textural characteristics of the natural zeolitic materials change with the metallic species that compensates for the charge in the zeolitic network. The  $\text{pH}_{\text{pzc}}$  varies with respect to the surface characteristics of the zeolitic materials. The clinoptilolite-rich tuff modified with Na, Fe, and Ag has an acidic surface and the mordenite-rich tuff modified with the same metallic species has a basic surface. The cationic composition of the zeolitic tuffs indicates that ion exchange could be the main mechanism responsible for manganese removal.

The time to reach equilibrium for Mn(II) sorption by the zeolitic materials depends on the nature of the zeolite and the ions that modified the networks. The pseudo-second order model describes the kinetic behaviour and the Freundlich model describes the isotherm for the Mn(II) sorption processes. When modified with silver, both zeolitic materials, clinoptilolite- and mordenite-rich tuffs, could be used for the removal of manganese from aqueous solutions, independent of their structural characteristics.

### Graphical Abstract



### Highlights

- The content of silver and iron is similar in both zeolite-rich tuffs.
- The textural characteristics of the zeolitic materials change with the metallic species.
- The  $\text{pH}_{\text{pzc}}$  varies with respect to the surface characteristics of the zeolitic materials.
- The Mn(II) sorption depends on the cations and structure of the zeolite.
- The Ag-modified zeolite-rich tuffs improve the Mn(II) sorption.

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