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SORPTION OF Cd(II), Ni(II) AND Zn(II) ON NATURAL, SODIUM-, AND ACID-MODIFIED CLINOPTILOLITE-RICH TUFF

Sorption of Cd^{2+}, Ni^{2+} and Zn^{2+} ions on natural (ZPCli), sodium modified (ZPCliNa) and acid modified (ZPCliH) zeolites have been investigated in function of the contact time, pH, and metal concentration by the batch technique. The characterization of ZPCli, ZPCliNa, and ZPCliH materials was performed using X-ray powder diffraction, scanning electron microscopy and energy dispersive X-ray spectroscopy techniques. The surface area (BET) and the pH_{pzc} were also determined. The pH in the point of the zero charge of ZPCli, ZPCliNa, and ZPCliH zeolites was 8.25, 8.00, and 2.05, respectively. The kinetic sorption data for ZPCli, ZPCliNa and ZPCliH were well fitted to the pseudo-second order model ($R^2 > 0.99$). The linear model described the Cd, Ni and Zn sorption isotherms for ZPCliH, while for ZPCliNa and ZPCliH it was the Freundlich model. The unmodified and modified zeolitic materials showed the highest sorption capacity for Cd^{2+}, lower for Zn^{2+} and Ni^{2+}.

1. INTRODUCTION

Many toxic heavy metals have been excessively discharged into the environment causing a serious soil and water contamination. Cadmium, nickel, and zinc are common metals used in several industrial activities such as mining, smelting, battery manufacturing, tanneries, petroleum refining, paint manufacturing, pesticides, pigment manufacturing, printing and photographic industries, among others [1, 2]. It is well known that heavy metals are non-biodegradable and tend to accumulate in organisms, causing

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various diseases and disorders [3]. These metals have been classified by the U.S. Environmental Protection Agency as a probable human carcinogens, and some regulations have been proposed to reduce the public health risks. The regulatory limits of cadmium, nickel and zinc in drinking water are 0.01, 0.2 and 5 mg/dm^3, respectively [4]. Numerous processes are available for removing dissolved metals, including precipitation, phytoextraction, ultrafiltration, reverse osmosis, and electrodialysis [5]. Ion exchange is considered a cost-effective method provided that low cost ion exchangers such as zeolites are used [6]. The clinoptilolite, in particular, has a high affinity for cadmium, nickel, and zinc [7, 8]. The sorption capacity of natural zeolite (clinoptilolite) for inorganic cations has been investigated [9]. The selectivity series of clinoptilolite in the sodium form has been determined by Zamzow et al. [10], as follows: Pb(II) > Cd(II) > Cs(II) > Cu(II) > Co(II) > Cr(III) > Zn(II) > Ni(II) > Hg(II).

Various researchers reported the use of natural and modified zeolites to remove inorganic compounds including heavy metals from wastewater [17, 11]. However, no investigations have been reported to compare the removal efficiency of metallic cations from aqueous solutions by unmodified or modified natural zeolites, considering their behavior in various reaction media (pH). Furthermore, the clinoptilolite-rich tuffs from different regions have specific sorption properties [7]. Therefore, the aim of this work was to evaluate the effectiveness of unmodified and modified Mexican clinoptilolite-rich tuff to remove Cd(II), Ni(II) and Zn(II) from aqueous media considering pH, the contact time and the concentration of heavy metals in solution to describe the sorption behavior and the selectivity of each zeolitic material under investigation.

2. MATERIALS AND METHODS

Materials. The adsorption experiments were performed on clinoptilolite-rich tuff from Puebla State (Mexico). The natural zeolite was sieved to obtain a grain size of 400 μm. Before modification, the zeolite was washed with distilled water three times for removing suspended materials; the solids were then dried in an electric oven at 100 °C for 12 h. The zeolitic sample was labeled as ZPCli.

Deionized water was used to prepare synthetic stock solutions (1000 mg/dm^3) of Cd(II), Ni(II), and Zn(II), using $3CdSO_4 \cdot 8H_2O$, $NiCl_2 \cdot 6H_2O$, and $ZnCl_2 \cdot 6H_2O$ salts, respectively. All reagents were purchased from J.T. Baker with purity more than 99.99%.

The ZPCli sample (25 g) was mixed with a sodium chloride solution (1.0 mol/dm^3) in a 250 cm^3 flask to ensure a better contact between phases. The mixture was placed in a mechanical shaker for 1 h at room temperature. The supernatant was decanted and this procedure was repeated four times with a fresh NaCl solution to promote the ion exchange process. Then, the sample was washed several times with distilled water until no chloride ions were detected in the washing solution (tested by AgNO$_3$). The Na-modified zeolitic material was dried at 100 °C for 12 h. The sample obtained from this process is referred as ZPCliNa.

A quantity of 25 g of ZPCliNa was refluxed with 500 cm^3 of 1 mol/dm^3 H$_2$SO$_4$ (with solid to liquid ratio equal to 1:20) for 4 h at 90 °C. The resulting zeolite was washed with distilled water several times until it was free of SO$_4^{2-}$ ions and dried at 100 °C in an electric oven for 12 h. This zeolitic sample was referred as ZPCliH.

pH in the point of zero charge (pH$_{PZC}$). The pH of the point of zero charge (pH$_{PZC}$) of ZPCli, ZPCliNa and ZPCliH samples were determined using the method described by Zaini et al. [12] and Ma et al. [13]: 0.10 g of each adsorbent were mixed with 50 cm^3 of 0.01 mol/dm^3 NaCl at different initial pH (pH = 2, 4, 6, 8, 10). The initial pH of the aqueous solution was adjusted by small addition of 0.1 mol/dm^3 HCl or 0.1 mol/dm^3 NaOH solutions. The suspensions were allowed to equilibrate for 72 h under mechanic agitation at 25 °C, then centrifuged at 5000 rpm for 10 min and the final pH of each supernatant was measured using a pH-meter.

Characterization. The X-ray diffraction (XRD) method was carried out by an APD 2000 PRO X-Ray diffractometer and the XRD patterns were recorded with a CuK$_\alpha$ radiation at λ = 1.5405 Å at 35 kV and 25 mA in the range of 2θ from 2° to 60°, with the scanning speed of 0.025 deg/s and step time 10 s. The mineral phases of the zeolite-rich tuff from Puebla (México) were identified by comparison with JCPDS cards.

Scanning Electron Microscopy (SEM) was used to determine the morphological and qualitative characteristics of the ZPCli, ZPCliNa and ZPCliH. The electron dispersive X-ray (EDX) analysis was performed on a scanning electron microscope (Hitachi S4500). The images were taken using the magnification of 1500×, current intensity of 30 pA, voltage of 10 kV and the work distance of 10.5 mm.

Nitrogen adsorption-desorption isotherm technique was used to determine the specific surface areas of clinoptilolite-rich tuffs. The measurements were obtained via a BELSORP MAX analyzer using N$_2$. The zeolitic sample was heated to 250 °C for 24 h, after the BET equation was applied for calculating the specific surface areas of ZPCli, ZPCliNa and ZPCliH; also the monolayer volume, total pore volume and mean pore diameter were calculated considering the sorption isotherms at relative pressures between 0.05 and 0.5.

Sorption. Batch type experiment was performed to determine the kinetics removal of Cd^{2+}, Ni^{2+}, and Zn^{2+} on ZPCli, ZPCliNa and ZPCliH. 0.1 g of each adsorbent was added to 10 cm^3 of 10 mg/dm^3 heavy metal solutions at pH from 2 to 10. The pH of the aqueous solution was adjusted by adding a small amount of HCl to acidify or NaOH to basify, using an Orion 3 Star pH-meter. The mixtures were placed in centrifuge tubes, reacting for 1440 min, taking aliquots at 5, 10, 30, 60, 120, 180, 240, 360, 720, 1440 min. After each contact time, the tubes were centrifuged at 4500 rpm for 5 min, and the Cd, Ni, and Zn concentrations were determined by the atomic absorption spectroscopy (Thermo Scientific iCE 3000 Series) at the wavelengths of 228.8, 232, and 213.9 nm, respectively.

The amount of Cd, Ni, and Zn adsorbed on natural and modified clinoptilolite was calculated using the mass balance expression:

$$q = \frac{(C_0 - C_t)V}{W}$$

(1)

where: q is the amount of Cd, Ni and Zn adsorbed in the natural and modified zeolites (mg/g), V is the volume of the solution (cm^3), W is the weight of the adsorbent (g), C_0 is the initial metal concentration (mg/dm^3) and C_t is the concentration at time t.

For adsorption isotherms, 0.1g of each adsorbent was mixed with 10 cm^3 of aqueous solutions with different concentrations of Cd(II), Ni(II) and Zn(II) (10, 20, 40, 80, 100, 150, 200, 300, 400, and 500 mg/dm^3) and shaken for 24 h at room temperature at pH 4. This pH was chosen in order to avoid the precipitation of metals, and also for the high yield shown at this value. The mixtures were centrifuged at 4500 rpm for 5 min and then decanted. The heavy metals in each supernatant were analyzed by atomic absorption spectroscopy (AAS) as mentioned before.

3. RESULTS AND DISCUSSION

3.1. pH OF THE POINT OF ZERO CHARGE (PH$_{pzc}$)

pH in the point of zero charge, pH$_{pzc}$, is the pH at which the curve pH$_{final}$ = fpH$_{initial}$ crosses the straight line that fits the points pH$_{final}$ = pH$_{initial}$ [14].Therefore, the pH$_{pzc}$
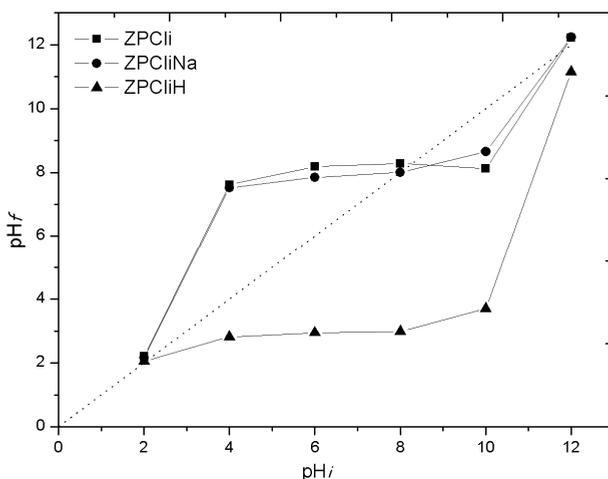
Fig. 1. The final pH (pH$_f$) as a function of the initial pH (pH$_i$)
for unmodified and modified natural zeolites

value was found at pH = 8.25 ±0.01 for ZPCli, while it was 8.00±0.01 and 2.05±0.01 for the ZPCliNa and ZPCliH, respectively (Fig. 1). The pH$_{PZC}$ decreased to a low value (from 8 to 2). Indeed this result can be explained by the dealumination phenomenon which promotes the decrease of the negative charge, consequently diminishes the number of cations and generate a very strong Lewis acid sites. Furthermore an increase of Si/Al is also expected [15].

3.2. CHARACTERIZATION

The X-ray diffraction (XRD) patterns (Fig. 2) analyzed by the MATCH program show the presence of clinoptilolite-Na phase (JPCDS 00-025-1349 card) in ZPCli, ZPCliNa and ZPCliH materials with the principal reflexions 2θ at = 9.80°, 22.36°, and 31.94°. Other component in a minor amount is also observed and identified at $2\theta = 26.56°$ which corresponds to quartz (JPCDS 01-085-0504). ZPCli was heated at 500 °C for 3 h, in order to confirm that it is not heulandite-Na. X-ray diffraction patterns of the clinoptilolite-rich tuff samples showed that modification of clinoptilolite with NaCl did not lead to significant structural changes. The reflexion positions are similar in both cases (ZPCli and ZPCliNa). However, the X-ray diffraction pattern of ZPCliH shows that some small reflexions disappeared at $2\theta = 20.35°$, 43.20°, 45.07°, 50.85° with respect to those observed for ZPCliNa. The intensity of reflexions at $2\theta = 22.36°$, 22.70°, 29.90°, and 31.91° decreased, and at $2\theta = 26.57°$ significantly increased after acid treatment.
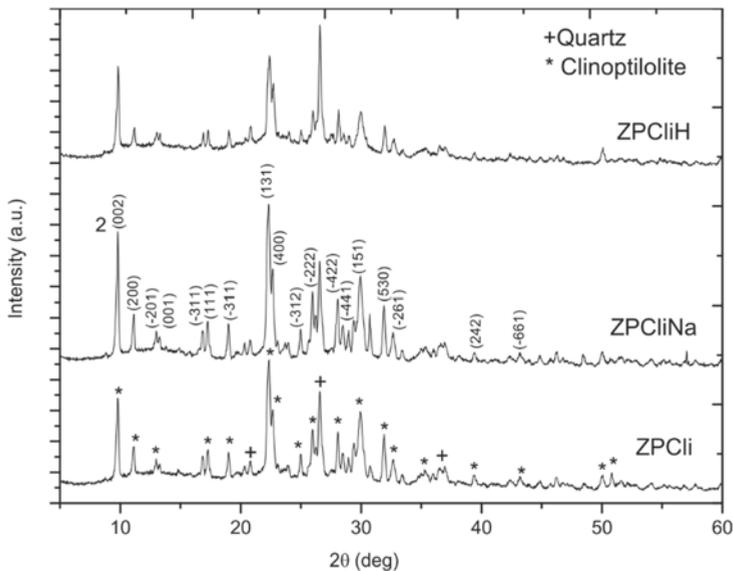
Fig. 2. X-ray diffraction patterns of the unmodified and modified natural zeolites

Figure 3 shows the crystals of ZPCli, ZPCliNa and ZPCliH, which are coffin and cubic-like exhibiting characteristic features of monoclinic symmetry. These results confirm those obtained by X-ray diffraction. Moreover, any change of surface morphology was noted after the treatment with NaCl and H_2SO_4, except the disappearance of a bright spot in the ZPCliH sample possibly associated with releasing Fe from the zeolite network under acidic conditions (Table 1).
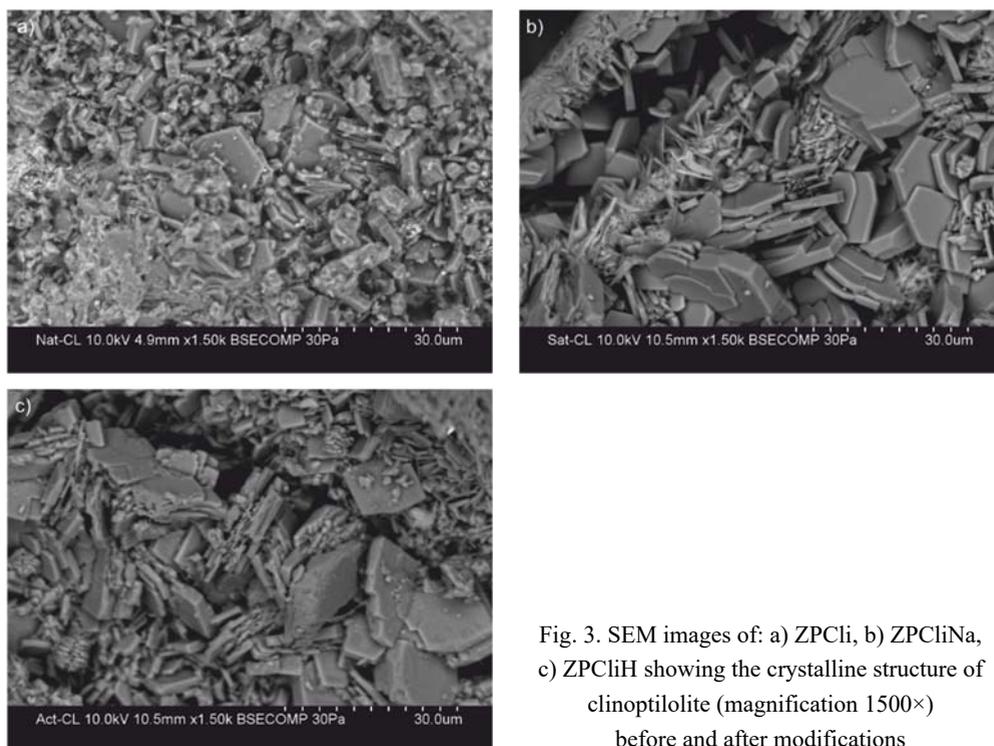
Fig. 3. SEM images of: a) ZPCli, b) ZPCliNa,
c) ZPCliH showing the crystalline structure of
clinoptilolite (magnification 1500×)
before and after modifications

T a b l e   1

Elemental composition of unmodified and modified natural zeolites

	O [%]	Na [%]	Al [%]	Si [%]	K [%]	Ca [%]	Fe [%]	S [%]	Si/Al
ZPCli	64.57±0.51	0.25±0.03	5.55±0.01	24.85±0.44	1.86±0.34	1.73±0.27	1.06±0.78	0.00	4.47
ZPCliNa	68.80±1.65	1.44±0.19	5.19±0.26	22.98±1.13	0.71±0.19	0.83±0.19	0.69±0.49	0.00	4.42
ZPCliH	65.73±2.79	0.00	4.2±0.39	28.46±3.13	0.61±0.32	0.48±0.31	0.39±0.12	0.07±0.07	6.77

After the treatment of the ZPCli with NaCl solution the sodium content increased 6 times, whereas it is decreased notably for K^+, Ca^{2+}, and Fe^{2+}. The acid treatment promotes the total elimination of sodium, and decreases the amount of the other cations,

which can be explained by introducing H^+ ions into zeolites. Furthermore a significant decrease of the aluminum content, and an increase of Si/Al ratio are noted, and that may affect the cation exchange capacity of the zeolitic material [16, 17].

<div align="right">T a b l e 2</div>

<div align="center">Textural parameters of the natural and modified zeolites</div>

Parameter	ZPCli	ZPCliNa	ZPCliH
Specific surface area ($a_{s,BET}$), m²/g	11.93	10.40	55.20
Mean pore diameter, nm	17.19	15.98	5.88
Total pore volume ($p/p_0 = 0.99$), cm³/g	5.1279×10^{-2}	4.17×10^{-2}	8.13×10^{-2}

The textural parameters of ZPCli and ZPCliNa are similar. However for ZPCliH, the total pore volume increases approximately 1.5 and 2 times and the surface area increases 4.5 and 5 times in comparison to ZPCliNa and ZPCli, respectively (Table 2). The mean pore diameter decreases 2.5 and 3 times in comparison to ZPCliNa and ZPCli, respectively. These results show that the modification of the ZPCli with H_2SO_4 caused a drastical change of the structure of the zeolitic material.

3.3. SORPTION

From Figure 4 it can be seen that sorption of Cd, Ni, and Zn metal ions on ZPCli, and ZPCliNa, increases rapidly with time up to 30 min (99 % uptake, except the pH = 2, with 30 %), and occurs more slowly afterwards, until that the equilibrium was reached. Although the behavior of ZPCliH differs from a metal to other at pH from 4 to 10, however the behavior at pH = 2 is similar (the equilibrium was reached at 30 min). It is important to mention that the sorption behavior of the Cd^{2+}, Ni^{2+} and Zn^{2+} is similar in the natural (ZPCli) and modified zeolites (ZPCliNa and ZPCliH) at pH of 2. In case of the sorption of Cd^{2+} on ZPCliH, the equilibrium is reached at 700 min considering pH 4 and 10, although the equilibrium is not observed at pH of 6 and 8. The sorption of ZPCliH for Ni^{2+} depends on the pH, and the highest efficiency is observed at pH 10. The equilibrium is reached between 300 and 400 min depending of the pH. The sorption of Zn^{2+} increased rapidly at pH = 10 and gradually at pH = 4, 6, and 8 then the equilibrium was reached after 720 min. Mathematical models that are used most frequently to describe the behavior of the sorption kinetics in batch system are the pseudo-first and pseudo-second order models [18, 19].

The pseudo-first-order kinetic model is described as:

$$\frac{dq_t}{dt} = k_1 \left(q_e - q_t \right) \tag{2}$$

where: q_t (mg/g) is the amount of metal ions adsorbed at time t (min), q_e (mg/g) is the amount adsorbed at equilibrium, k_1 (1/h) is the rate constant of first-order.
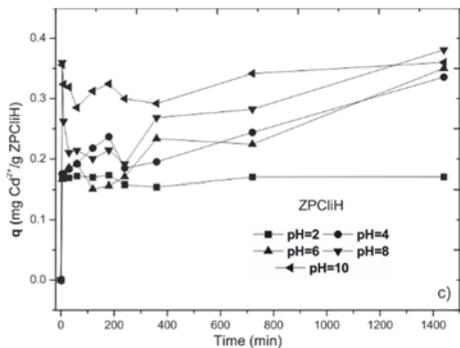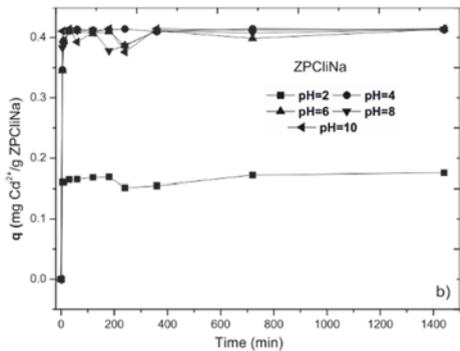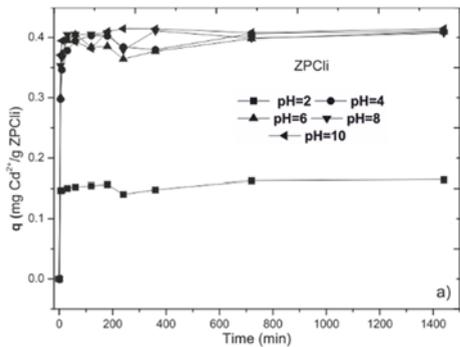
Fig. 4. Sorption of Cd^{2+} on natural (a),
and modified (ZPCliNa (b), ZPCliH (c)) zeolites
in function of time
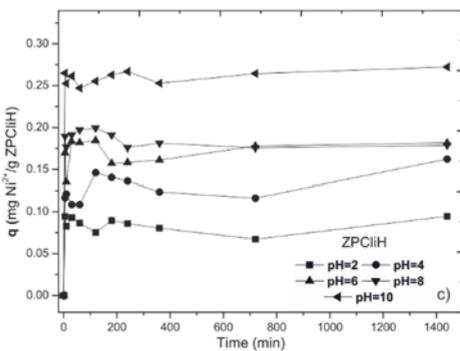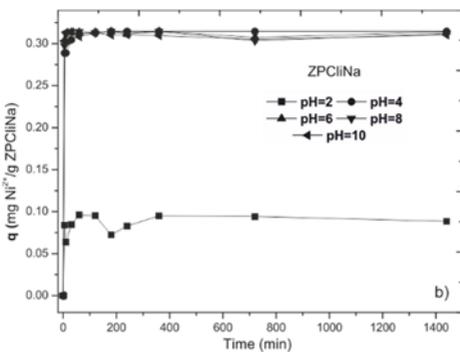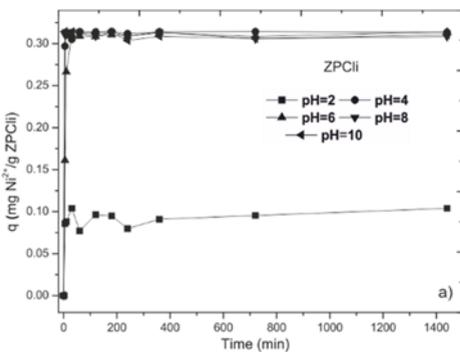
Fig. 5. Sorption of Cd^{2+} on natural (a),
and modified (ZPCliNa (b), ZPCliH (c)) zeolites
in function of time
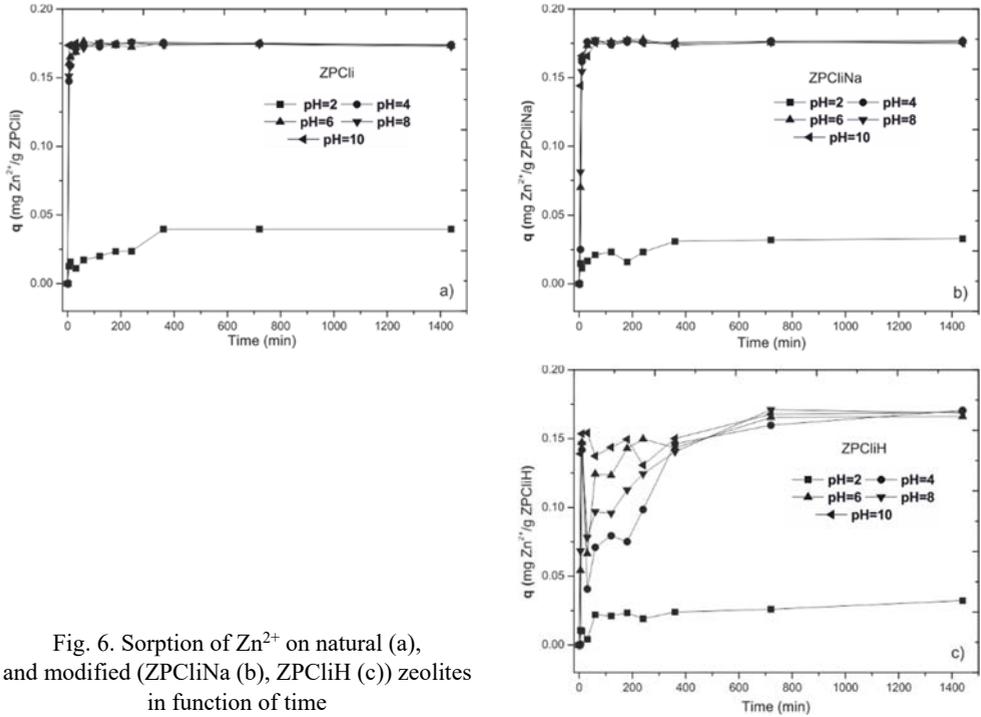
Fig. 6. Sorption of Zn^{2+} on natural (a),
and modified (ZPCliNa (b), ZPCliH (c)) zeolites
in function of time

After integration between boundary conditions (from $t = 0$ to t, and from $q_t = 0$ to q_e), the equation becomes:

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t \tag{3}$$

where: q_e and k_1 can be determined from the intercept and slope of the plot, respectively. The pseudo-second order kinetic model is based on the sorption capacity of the solid phase and expressed as:

$$\frac{dq_t}{dt} = k_2\left(q_e - q_t\right)^2 \tag{4}$$

where: k_2 (g/(mg·h) is the rate constant of the second order reaction.

For boundary condition (from $t = 0$ to t, and from $q_t = 0$ to q_e), the equation becomes:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{5}$$

The plot of t/q_t vs. t should give a straight line if the pseudo-second order kinetic model is applicable, and q_e and k_2 can be determined from the plot.

The experimental data were fitted with the two models mentioned above; the best fit was obtained using the pseudo-second order model.

T a b l e 3

Parameters of the pseudo-second order kinetic model for the sorption of metallic ions on natural and modified zeolites at different pH

pH	Zeolite	Parameters of the model			pH	Zeolite	Parameters of the model		
		k_2 [g/(mg·h)]	q_e [mg/g]	R^2			k_2 [g/(mg·h)]	q_e [mg/g]	R^2
		Cd^{2+}					Ni^{2+}		
2	ZPCli	18.188	0.042	0.98	2	ZPCli	27.102	0.103	0.99
	ZPCliNa	29.430	0.034	0.98		ZPCliNa	97.612	0.090	0.99
	ZPCliH	16.420	0.033	0.99		ZPCliH	29.782	0.089	0.96
4	ZPCli	360.116	0.174	0.99	4	ZPCli	683.400	0.314	1
	ZPCliNa	58.355	0.177	0.99		ZPCliNa	364.732	0.314	1
	ZPCliH	3.879	0.179	0.81		ZPCliH	11.111	0.1542	0.96
6	ZPCli	963.847	0.174	0.99	6	ZPCli	72.640	0.3135	0.99
	ZPCliNa	185.693	0.176	0.99		ZPCliNa	269.430	0.312	0.99
	ZPCliH	11.995	0.169	0.67		ZPCliH	4.815	0.181	0.99
8	ZPCli	671.056	0.174	0.98	8	ZPCli	178.662	0.307	0.99
	ZPCliNa	270.463	0.175	0.99		ZPCliNa	299.780	0.311	0.99
	ZPCliH	5.933	0.174	0.77		ZPCliH	86.522	0.177	0.99
10	ZPCli	845.922	0.175	0.99	10	ZPCli	284.240	0.309	0.99
	ZPCliNa	346.057	0.176	0.99		ZPCliNa	195.28	0.309	0.99
	ZPCliH	16.699	0.170	0.98		ZPCliH	16.962	0.268	0.96
		Zn^{2+}							
2	ZPCli	30.208	0.164	0.87					
	ZPCliNa	28.323	0.175	0.90					
	ZPCliH	62.876	0.169	0.89					
4	ZPCli	50.372	0.410	0.99					
	ZPCliNa	543.404	0.413	0.99					
	ZPCliH	2.207	0.348	0.96					
6	ZPCli	14.734	0.408	0.99					
	ZPCliNa	38.347	0.412	0.99					
	ZPCliH	1.529	0.338	0.99					
8	ZPCli	9.452	0.444	0.99					
	ZPCliNa	18.054	0.414	0.99					
	ZPCliH	1.829	0.3847	0.98					
10	ZPCli	11.083	0.416	0.99					
	ZPCliNa	8.534	0.417	0.99					
	ZPCliH	4.040	0.364	0.99					

The values of the rate constants and amounts of Cd, Ni, and Zn adsorbed on the ZPCli, ZPCliNa and ZPCliH at the equilibrium as well as the parameters of the equations are presented in Table 3. The adsorption of Cd^{2+}, Ni^{2+}, and Zn^{2+} onto ZPCli, ZPCliNa, and ZPCliH fitted well with to the pseudo-second order kinetic model ($R^2 > 0.99$). The kinetic constant rate (k_2) for ZPCliH was lower than those for ZPCli and ZPCliNa at all pH (except pH = 2), which demonstrates the effect of the acid treatment on the heavy metal adsorption behavior due to the dealumination of the zeolitic material (Table 1). Moreover, the values of q_e for Cd, Ni and Zn were similar to the experimental values determined for other the materials fulfilling the pseudo-second order kinetic model.

pH of the contact solution is one of the most important variables in sorption processes [20]. Figure 7 shows the retention of Ni^{2+}, Zn^{2+}, and Cd^{2+} on the modified and unmodified zeolitic materials at various pH at 1440 min corresponding to the last experimental point of the adsorption processes and in where the plateau is maintained. The data were taken from Fig. 1 for comparison.
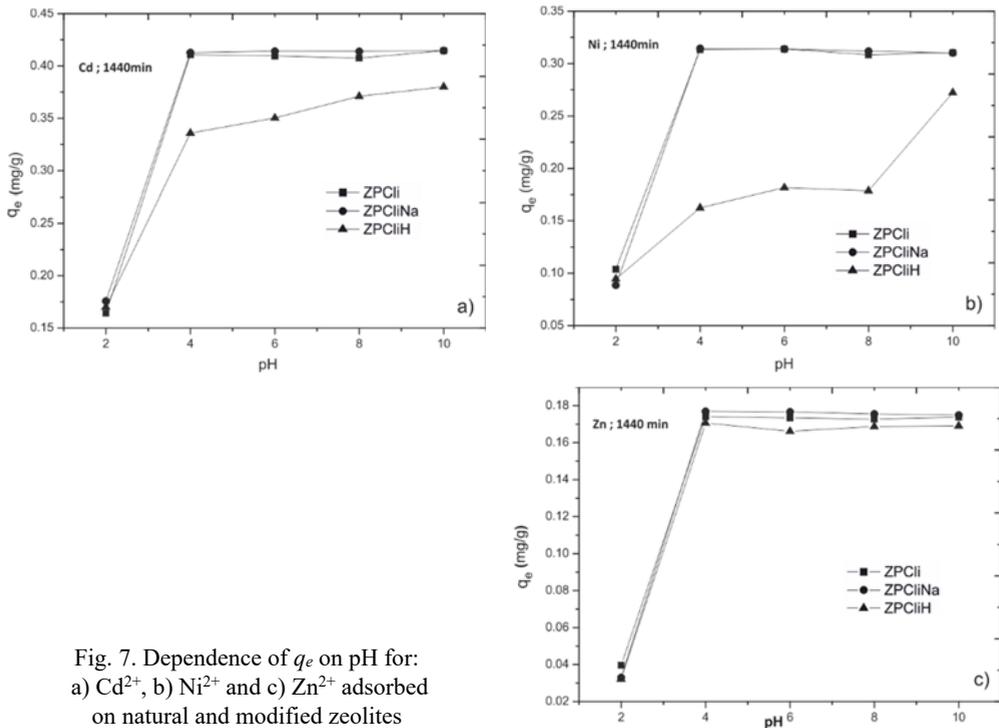
Fig. 7. Dependence of q_e on pH for:
a) Cd^{2+}, b) Ni^{2+} and c) Zn^{2+} adsorbed
on natural and modified zeolites

The q_e value of Cd^{2+}, Ni^{2+}, and Zn^{2+} adsorbed on zeolitic materials depends on pH and the type of modification of ZPCli. For Cd^{2+} at pH 2, q_e was similar (around 0.15 mg/g) for ZPCli, ZPCliNa and ZPCliH. However, this value drastically increased at pH from 4 to 10, up to 0.42 mg/g for ZPCli and ZPCliNa. For ZPCliH, q_e gradually increased, and at

pH 10 the maximum sorption was 0.36 mg Cd/g. The q_e for Ni sorbed on ZPCli, ZPCliNa and ZPCliH was 0.1 mg/g at pH 2. This amount was 0.31 mg/g for pH from 4 to 10 than at pH 2 for ZPCli and ZPCliNa). However, for ZPCliH, q_e for Ni was similar at pH between 4 and 8 (0.16 mg/g) and at pH 10 increased up to 0.28 mg/g. q_e for Zn sorbed on ZPCli, ZPCliNa and ZPCliH was 0.03 mg/g at pH 2. It increased at pH from 4 to 10 up to 0.18 mg/g for the three zeolitic materials. These results show that the zeolite modified with sodium (ZPCliNa) has similar ion exchange behavior with respect to unmodified zeolite (ZPCli) in contrast with the ZPCliH, which presents less sorption capacity.Figure 8. Distribution diagrams of Cd^{2+}, Ni^{2+}, and Zn^{2+} ions in function of pH
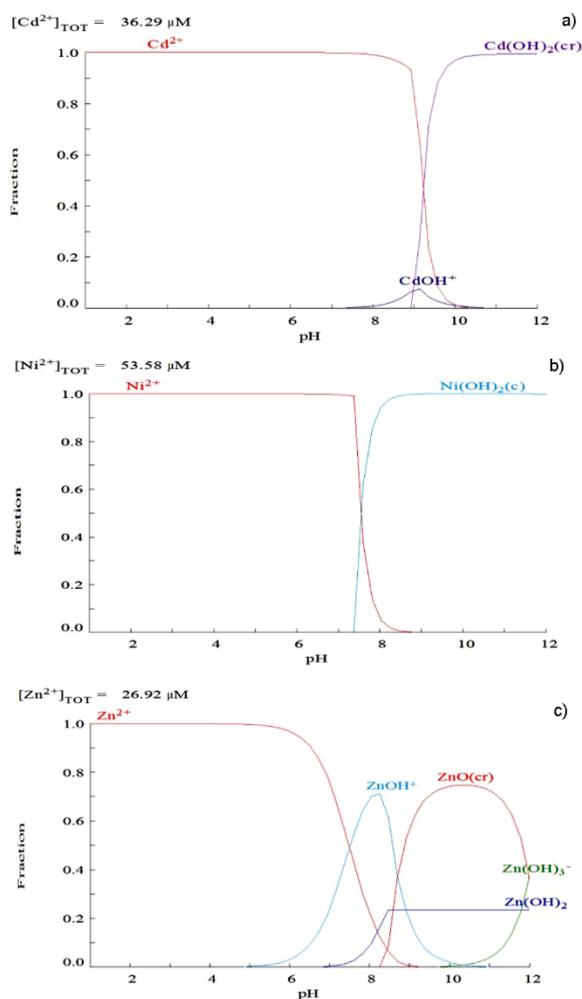
Fig. 8. Distribution diagrams of Cd^{2+}, Ni^{2+}, and Zn^{2+} ions in function of pH

According to the pH$_{PZC}$ data, the metallic solutions were basified with ZPCli and ZPCliNa after the sorption processes at pH 4 and 6, which promote the formation of hydroxides, as the chemical equilibrium diagrams for the three metals in aqueous solution that are shown in Figure 8. The results obtained above for Ni^{2+} and Zn^{2+} indicate that the sorption could be performed by two mechanism: a) precipitation on the surface of ZPCli and ZPCliNa from initial pH 4, and b) ion exchange between the native ions from the zeolite in the case of ZPCli and Na^{+} from ZPCliNa with Ni^{2+} or Zn^{2+} ions from the aqueous media. The sorption of Cd^{2+} on ZPCli and ZPCliNa is the highest and it is possible that the ion exchange could be the dominant mechanism because the hydrolysis of this ion begins at pH 8. The metallic solutions are acidified with ZPCliH, after the sorption processes and the final pH of the solution was 2.05. Above this value, the surface is charged negatively which promotes both the adsorption of the cation by coulombic interactions (Ni^{2+}, Zn^{2+}, and Cd^{2+}) and the ion exchange [21]. Although, the adsorption capacities of the three zeolitic materials at pH 2 are the lowest because during adsorption at lower pH, H^{+} ions compete with the metallic ions in solution (Cd^{2+}, Ni^{2+} and Zn^{2+}) for the ion exchange sites into the zeolite network [11, 16, 22].

The H^{+} competence is well noted for the ZPCliH. The adsorption capacity increases upon increasing initial pH. Thus, the high acidity may also have a beneficial effect to avoid the hydrolysis of the metallic ions in solution. Hydration is followed by hydrolysis, according to the following two-ray reversible reaction, giving acidic properties to heavy metal solutions. The following equilibrium can be considered:

$$[M(H_2O)_x]^{2+} + H_2O \leftrightarrow [M(H_2O)_{x-1}(OH)]^{+} + H_3O^{+} \tag{6}$$
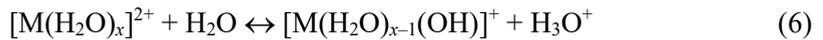
In low acidic media, the above equilibrium is shifted to the left and more highly charged metal complexes are formed which could promote the adsorption. The radius of the hydrated metal complex ($[M(H_2O)^{-1}(OH)]^{+}$) is smaller than that of the hydrated metal ion $[M(H_2O)_x]^{2+}$, thus the radius of the hydrated metal complex had a higher mobility than the hydrated metal ion.

The adsorption capacities of the ZPCli, ZPCliNa and ZPCliH with respect to Cd^{2+}, Ni^{2+} and Zn^{2+} ions, were determined (Fig. 9) based on the linear, Langmuir and Freundlich models to describe.

The linear model is described by the following equation:

$$q_e = K_d C_e \tag{7}$$

where: q_e (mg/g) is the adsorbate concentration in the solid at equilibrium, C_e (mg/dm^3) is the concentration of the adsorbate in the liquid phase, K_d is the equilibrium distribution coefficient.
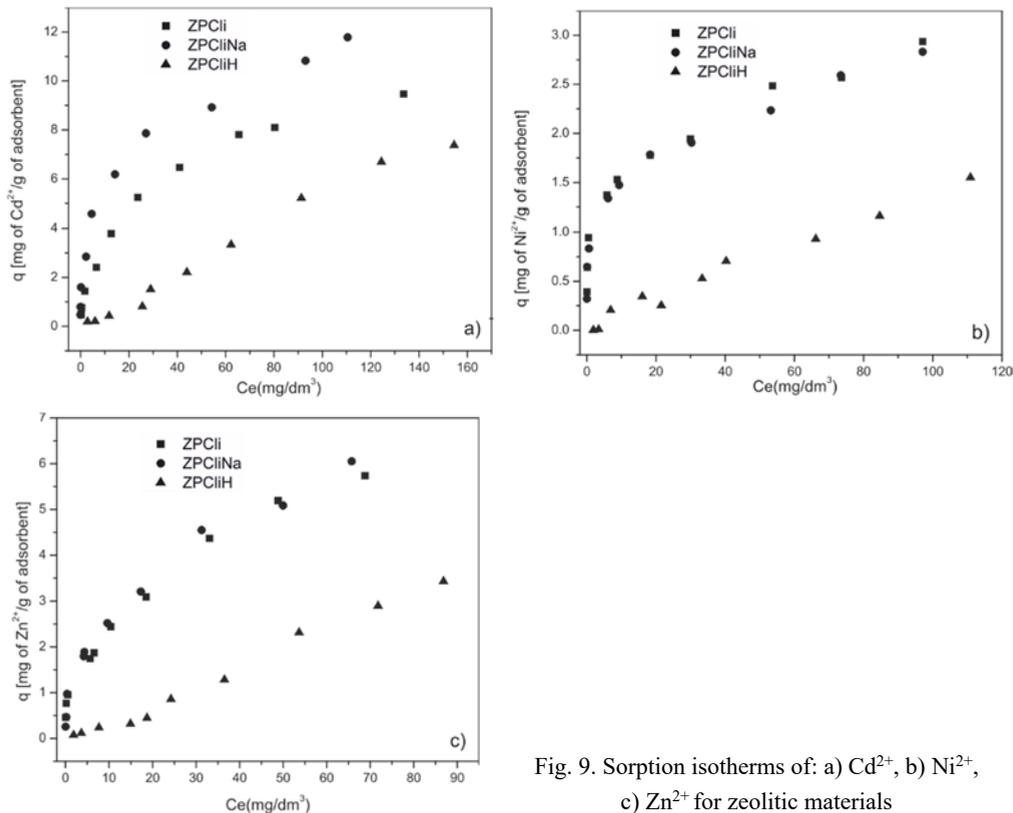
Fig. 9. Sorption isotherms of: a) Cd^{2+}, b) Ni^{2+}, c) Zn^{2+} for zeolitic materials

The Langmuir isotherm is represented as:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \qquad (8)$$

where: q_e is the amount of adsorbate adsorbed at equilibrium (mg/g); C_e is its equilibrium concentration in the solution (mg/dm^3), K_L is the Langmuir constant related to the affinity of the binding site (dm^3/mg), q_m is the maximum amount of solute adsorbed (mg/g). The Langmuir equation can be described by a linear equation as follows:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L C_e q_m} \qquad (9)$$

The constants q_m and K_L were obtained from the slope and intercept of the plot of $1/q_e$ versus $1/C_e$.

The Freundlich isotherm describes adsorption on a heterogeneous surface with a non-uniform distribution of energy of adsorption:

$$q_e = K_F C_e^{1/n} \tag{10}$$

where K_F $(mg/g)(dm^3/g)^{1/n}$ and n are the constants for a given adsorbate and adsorbent at constant temperature. If $n > 1$, adsorption is considered favorable. The linearized form of the Freundlich sorption isotherm is:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{11}$$

The constants K_F and n were obtained from the plot of $\ln q_e$ versus $\ln C_e$. The experimental data fitted well to linear or Freundlich isotherms depending on the zeolitic material. The obtained parameters are presented in Table 4.

Table 4

Parameters obtained from linear and Freundlich models
for the sorption of Cd^{2+}, Ni^{2+} and Zn^{2+} on zeolitic materials

Linear isotherm			
Ion	Adsorbent	K_d [dm^3/g]	R^2
Cd^{2+}	ZPCliH	0.0512	0.985
Ni^{2+}		0.0143	0.978
Zn^{2+}		0.0394	0.981
Freundlich isotherm			
Ion	Adsorbent	K_F [$(mg/g)(dm^3/g)^{1/n}$]	n	R^2
Cd^{2+}	ZPCli	1.206	2.293	0.995
	ZPCliNa	2.872	3.584	0.992
Ni^{2+}	ZPCli	1.054	5.025	0.988
	ZPCliNa	0.854	4.366	0.987
Zn^{2+}	ZPCli	1.0286	2.967	0.972
	ZPCliNa	1.0365	2.493	0.979

The data on sorption of Cd^{2+}, Ni^{2+} and Zn^{2+} onto ZPCliH fitted well to linear isotherm ($R^2 > 0.978$). The R^2 values for data fitted to Langmuir and Freundlich isotherms, were lower than 0.970.

The equilibrium distribution coefficient for Cd^{2+} in ZPCliH is 3.6, being 1.3 times higher than those for Ni^{2+} and Zn^{2+}. This shows that Cd^{2+} is preferentially removed from the aqueous media with respect to Ni^{2+} and Zn^{2+} adsorbed onto ZPCli modified with

H$_2$SO$_4$ (ZPCliH). However, it is important to consider the dealumination of the zeolitic material and the losses of the cation exchange capacity in comparison with ZPCli and ZPCliNa (Table 1). The selectivity of the zeolitic material for each metallic cation is:

$$K_{d_{Cd^{2+}}} > K_{d_{Zn^{2+}}} > K_{d_{Ni^{2+}}}$$

pH$_{pzc}$ (2.05) of ZPCliH is another parameter that can play a role in its capacity to adsorb these ions, as was mentioned before (Fig. 1). It seems that the specific surface area (Table 2) has no significant meaning in the sorption processes. The sorption data for Cd^{2+}, Ni^{2+} and Zn^{2+} onto ZPCli and ZPCliNa fitted well to the Freundlich isotherm with $R^2 > 0.972$. The R^2 values for the linear model were lower than 0.690.

Figure 9 shows that ZPCliNa has a higher Cd^{2+} sorption capacity than ZPCli, and this result is in agreement with the K_F value that is 2.4 times greater for ZPCliNa than that for ZPCli. However, the sorption capacity of both zeolitic materials is similar for Ni^{2+} and Zn^{2+}, although the selectivities for Ni^{2+} and Zn^{2+} differ from each other. This means that ZPCli and ZPCliNa are more selective for Zn^{2+} than Ni^{2+} according to the values of their adsorption capacities which are 6 and 3 mg/g, respectively (Fig. 9). The K_F values confirm the similarity in the Ni^{2+} and Zn^{2+} sorption behavior for both ZPCli and ZPCliNa.

The Freundlich constant K_F follows the order:

$$K_{F_{Cd-ZPCliNa}} > K_{F_{Cd-ZPCli}} > K_{F_{Ni-ZPCli}} > K_{F_{Zn-ZPCliNa}} > K_{F_{Zn-ZPCli}} > K_{F_{Ni-ZPCliNa}}$$

The value of the parameter n reveals that the sorption processes were favorable in all cases ($n > 1$, Table 4). Similarly as for ZPCliH, the pH$_{pzc}$ value for ZPCli and ZPCliNa (around 8) can play a role in their capacity to adsorb these metallic ions.

Table 5

K_F parameter obtained from the Freundlich isotherm to describe
the Cd^{2+}, Ni^{2+} and Zn^{2+} sorption on natural zeolites

Clinoptilolite	Region of provenance	Metallic ion	K_F [(mg/g)(dm^3/g)$^{1/n}$]	Reference
Treated with NaCl	Chihuahua, Mexico	Cd^{2+}	0.6831	[23]
Treated with HCl and NH$_4$Cl	Sokyrnytsya, Ukraine		0.6359	[24]
Treated with CaCl2	Firouzkoh, Iran		0.024	[25]
Treated with HCl/NH$_4$Cl	Sokyrnytsya, Ukraine	Ni^{2+}	0.4463	[24]
Wwithout treatment	Manisa, Turkey		0.676	[26]
Ttreated with NaCl	Manisa-Gördes, Turkey	Zn^{2+}	6.3	[27]

It is important to mention that the parameter K_F obtained for the experimental data fitted to the Freundlich isotherm for Cd^{2+} sorption on ZPCliNa (clinoptilolite from Pue-

bla, Mexico in its sodium form) is notably different than those obtained for clinoptilolites from Chihuahua (Mexico), Sokyrnytsya (Ukraine) and Firouzkoh (Iran) previous treated with NaCl, HCl/NH$_4$Cl and CaCl$_2$ solutions (Table 5). However, K_F for the sorption of Ni^{2+} on ZPCliNa is slightly higher than those obtained for clinoptilolites from Sokyrnytsya (Ukraine) and Manisa (Turkey) and finally this parameter for the sorption of Zn^{2+} on ZPCliNa is lower than that obtained for clinoptilolite from Manisa-Gördes, (Turkey). As is seen, the sorption of metal ions depends of several factors such as the provenance of each natural zeolite, the treatment of zeolitic material before the sorption and the type of the heavy metal in to be adsorbed.

4. CONCLUSIONS

The major component of the zeolite-rich tuff from Puebla State, Mexico, is clinoptilolite and quartz in a minor amount. The material is a potassium-calcium zeolite. The dealumination of the natural zeolite (ZPCli) occurs after treatment with H$_2$SO$_4$ to obtain ZPCliH. The pH$_{pzc}$ is higher than 7 for ZPCli and for the sodium-modified zeolite (ZPCliNa) and lower than 7 for ZPCliH.

Each adsorption system reached the equilibrium at different time depending on the zeolitic material and the initial pH of the metallic solution. The equation of the pseudo--second order describes well the kinetic sorption behavior and the rate constant (k_2) for Cd^{2+} is the highest in all the pH range and each zeolitic materials.

ZPCli and ZPCliNa present higher sorption capacities for Cd^{2+}, Ni^{2+} and Zn^{2+} than ZPCliH. The selectivity of each zeolite follows the same order: Cd^{2+} > Zn^{2+} > Ni^{2+}. The experimental data of the sorption isotherms fit to linear model for ZPCliH and Freundlich model for ZPCli and ZPCliNa. The K_d parameter varies for particular ions and K_F and $1/n$ depend on both the nature of the ion and the treatment of the natural zeolite.

The proposed mechanisms responsible for the sorption of the metallic ions onto the zeolitic materials are ion exchange and precipitation on the surface considering the pH of the aqueous media and the pH$_{pzc}$ of each unmodified and modified natural zeolite.

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