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# Comparison of lead removal from aqueous solution between natural-, sodium-, and acid-modified clinoptilolite-rich tuffs

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ABSTRACT

In this paper, the sorption behavior of lead by unmodified and modified natural zeolites is discussed considering, the structural characteristics of each zeolitic material, the contact time, the initial concentration of Pb (II) in solution, the dosage of the adsorbents and the initial pH value. The characterization of all sorbents was performed using X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). The surface area (BET) and the $pH_{pzc}$ measurements were also determined. The contact between the Pb(II) solutions and the zeolites were done in a batch system. Mathematical models (pseudo-first and pseudo-second-order) were employed to describe the Pb(II) kinetic adsorption by natural, sodium, and acid-modified clinoptilolite-rich tuffs as well as Langmuir and Freundlich models to analyze the adsorption isotherms. It was found that the percentage of extra red cations from natural zeolite (Nat-CL) changes after contact with NaCl and $H_2SO_4$ solutions to obtain the sodium and acid forms (Na-CL and H-CL). The acid treatments of the natural zeolite promote the dealuminization of the material and the $pH_{pzc}$ drastically varied. The pseudo-second-order kinetic model best describes the sorption behavior and the $k_2$ diminished when the concentration of the lead in solution increases from 10 to 100 mg/L. The experimental data of the isotherms fitted to the Langmuir and Freundlich isotherms and the $q_m$ and $K_F$ are 2.6 and 15.2 times higher for Na-CL than for H-CL, respectively. The variation of kinetic rate constant $k_2$ (g/mg min) as a function of the adsorbent mass presents an exponential behavior for Nat-CL and Na-CL, whereas for H-CL, $k_2$ increase linearly with amount of adsorbent. The initial pH of the Pb solutions affect on the time to reach the $Pb^{2+}$ sorption equilibrium, the percentage of Pb sorbed in this condition. The mechanism involved on the sorption of Pb(II) by the Nat-CL and Na-CL are ion exchange and precipitation on the surface. In the case of H-CL, only an ion exchange could be possible.

*Keywords:* Lead; Sorption; Natural zeolites; Adsorption capacity; Kinetic

## 1. Introduction

Lead has been recognized one of the toxic heavy metals with an important potential hazard to humans and the environment. Lead and lead compounds have been used in a many variety of products including paint, ceramics, pipes and plumbing materials, solders, gasoline, batteries, ammunition, and cosmetics [1]. While it has some beneficial uses, nevertheless, large amounts may cause toxicity to humans and animals causing of health effects. According to the World Health Organization and Environmental Pro-

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tection Agency, the maximum permissible limit in drinking water and wastewater is approximately 0.05 mg/L [2,3]. Generally, heavy metals are highly toxic and tend to accumulate in living organisms because are not biodegradable. Therefore, they must to treat heavy metal containing wastewaters before being discharged into the environment.

Traditional techniques are commonly applied in removing heavy metals from industrial effluents including precipitation with chemical and electrochemical methods [4,5]. However, the principal problem of this treatment is the production of the large amount of metallic sludge, making metal recovery difficult and increase the pollution load on the environment [6]. Other methods that are being used to remove heavy metal ions include ion-exchange, adsorption, membrane filtration, electrochemical treatment technologies [7]. Among all water purification methods, ion exchange treatment is the most commonly used because it can reduce heavy metals to very low levels.

Natural zeolites are crystalline aluminosilicates consisting of molecular-sized pores and channels. These microporouse structures are made of three dimensional framework of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra, linked by sharing oxygen atoms. The partial substitution of $Si^{4+}$ by $Al^{3+}$ results the negative charge in the structure, which is compensated by the hydrated cations from alkali and alkaline earth cations ($Na^+$, $K^+$, $Ca^{2+}$ or $Mg^{2+}$) [8]. The crystalline micro porous of natural zeolites and their strong affinity for many heavy metals, have been used these materials as adsorbents and ion-exchanger for environmental remediation processes, particularly for water and soil purification [9].

There are reported papers in the literature that shows the capability of the natural zeolites to remove heavy metals from water because their cation exchange capacities. However, the chemical speciation is very important according with the pH of the aqueous media [10]. Furthermore, the selectivity of natural zeolites is dependent of dehydration energy of cations, diffusion coefficient and the pH where the precipitation of hydroxides is obtained [11]. The maximum adsorption capacities of Pb (II) reported by Ghahfarokhi et al., were 52.6 mg/g using a natural zeolite from Siah-Zagh mine of Semnan Province [12].

It was reported that other factor which affect the Pb(II) sorption by natural zeolites is the grain sizes. Clinoptilolite in power is more effective than granular clinoptilolite and the sorption of lead increases when the pH of the solution increases from 1 to 4 [13].

Several methods were used in order to improve the physical and chemical properties of naural zeolite as acid treatment, ion exchange and surfactant functionalization [14–16]. It can remove impurities that block pores in natural zeolites by acid treatment, and progressively eliminate cations to change into proton-form [14,17,18]. It is important to mention that the acid treatment of the natural zeolites promote a higher specific surface area with respect to those non modified zeolitic materials [19]. Therefore, the aim of this work was to describe the removal behavior of Pb(II) from aqueous media by the natural, sodium, and acid-modified clinoptilolite-rich tuff to compare their sorption for this heavy metal considering structural changes of the zeolitic network promoted by the contact with a strong acid solution. Therefore the novelty of this paper was to know the effect of acid treatment on the physicochemical properties of a zeolitic material for the sorption of $Pb^{2+}$ taking in account that it could be content in acidic wastewater among them mining effluents and lead acid battery.

## 2. Materials and methods

### *2.1. Materials and reagents*

Clinoptilolite rich-tuff used in this work was collected from a deposit located in the state of Puebla (Mexico). The starting material was sieved to obtain a grain size of 40 mesh and washed with distilled water to remove the water-soluble impurities. This sample (Nat-CL) was then dried in the oven at 80°C for 24 h.

#### *2.1.1. NaCl modification*

The conversion of natural zeolite to a homo-ionic or near homo-ionic state has been found to improve ion exchange capacities and performance [20,21]. Near sodium form of clinoptilolite sample (Na-CL) was prepared by stirring 30 g of Nat-CL and 200 mL of NaCl solution (1.0 M) in a 250 $cm^3$ flask. The mixture was agitated for 1 h at room temperature. The supernatant was discarded and replaced with a fresh solution of NaCl [22]. This procedure was repeated four more times and after that, the sample was washed for several times with deionized distilled water until $Cl^-$ free in the washing solution (tested by $AgNO_3$). Treated zeolite was dried at 80°C for 24 h.

#### *2.1.2. $H_2SO_4$ modification*

The H-form of clinoptilolite (H-CL) was obtained treating 25 g of Na-CL sample with 500 mL of $H_2SO_4$ 1 M for 4 h at 90°C. Then, the acid solutions were decanted and the solid residue was washed several times with deionized water until the pH reached values near to 5. The resulting acidic zeolite was then dried at 80°C in an electric oven for 24 h.

The deionized water was used to prepare the required concentrations of Pb considering the $PbCl_2$ salt (JT Baker, 99.99%).

### *2.2. Characterization*

X-ray diffraction (XRD) patterns of natural and modified zeolites were obtained by X-ray diffraction (XRD) using an APD 2000 PRO X-Ray diffractometer with CuKα radiation. Measurements were done in the 2θ range of 2° to 60°, with the scanning speed of 0.025 deg $s^{-1}$ and 10 s scanning time per step.

The morphology and the elemental chemical composition of the materials were performed by using a scanning electron microscopy combined with X-ray energy dispersive spectrometer (SEM/EDS HITACHI S-3400N).

The surface area and mean pore diameter of the samples were measured by the $N_2$ adsorption-desorption isotherm technique using the Brunauer–Emmett–Teller (BET) method (BELSORP-28SA equipment).

The pH of the point of zero charge ($pH_{PZC}$) of Nat-CL, Na-CL, and H-CL samples were determined using the method described by Zaini et al. [23] and Rojas-Pavón et al. [24]. 0.10 g of each adsorbent were mixed with 50 mL of 0.01 M NaCl adjusted to different initial pH values ($pH_{initial}$ = 1.0, 2.0, 2.5, 3.0, 3.5, 4, 6, 8, 10). The suspensions were allowed to equilibrate for 72 h under mechanic agitation at 25°C, decanted and the final pH of each remaining solution was determined with the ThermoElectron Orion 4 Star pH-meter. The $pH_{pzc}$ is the point where the curve $pH_{final}$ *vs.* $pH_{inital}$ crosses the line $pH_{initial} = pH_{final}$ [25].

### 2.3. Sorption process

Batch mode experiments were carried on to determine the Pb(II) sorption by Nat-CL, Na-CL, and H-CL. The experiments to obtain the kinetic parameters were conducted as follows: 0.1 g of each sorbent was added to 10 mL of $PbCl_2$ solutions at pH = 2.0 which concentrations varied from 10 to 100 mg/L. The mixtures were placed in centrifuge tubes and shaken in a rotary shaker for contact times ranging from 5 min to 24 h. After each specific contact time, the tubes were centrifuged at 3500 rpm for 2 min to separate the phases. The concentration of lead metal was determined using a flame atomic absorption spectroscopy (AAS, Thermo Scientific iCE 3000 Series). In order to ensure the truthfulness of experiment results, all experiments were made by duplicate.

The amount of Pb(II) sorbed per unit mass of the zeolitic materials was evaluated by using the following equation:

$$qt = \frac{(C_0 - C_t)}{m} V \tag{1}$$

where $C_0$ (mg L$^{-1}$) and $C_t$ (mg L$^{-1}$) are the initial and final metal concentration in solution, respectively, $V$ is the volume of aqueous phase (L) and $m$ is the mass of adsorbent (g).

The effects of (i) Pb(II) initial concentration (isotherms), (ii), initial pH and (iii) adsorbent dosage, on the sorption by Nat-Cl, Na-CL and H-CLI were also performed by a similar procedure described above considering the experimental conditions presented on Table 1. It is important to mention that the variation of pH is one of the significant parameters in the sorption of metal species by solids [26], because the ionic state of metal ions in solution is strongly depends on the pH value in solution and also can affect the surface electric charge of the adsorbent which is important for the electrostatic adsorption of ions and colloids [27].

Table 1
Experimental conditions for parameters tested

| Parameters | Time (min) | $C_i$ (mg/L) | $pH_i$ | Adsorbent dosage (g) |
|---|---|---|---|---|
| Initial concentration | 1440 | 10–500 | 2 | 0.1 |
| Initial pH | 30–360 | 100 | 2–10 | 0.1 |
| Adsorbent dosage | 1440 | 100 | 2 | 0.1–1.0 |

## 3. Results and discussion

### 3.1. Characterization

#### 3.1.1. XRD

The powder XRD results of the Nat-Cl, Na-Cl and H-CL samples demonstrate that natural and modified clinoptilolite present a similar pattern with the main reflexions at 2θ = 9.80°, 11.14°, 22.36°, and 31.94°, which correspond to the crystalline structure reported in the literature and in X-ray data file (JPCDS 00-025-1349 card) [28,29]. Minor amounts of quartz at 2θ = 26.56 (JPCDS 01-085-0504) was also found. A comparative analysis of the XRD pattern showed no significant changes in the positions of the most reflexions of the natural and modified clinoptilolite, which indicate that the zeolite structure does not change [29]. However, slight decrease can be observed in the relative intensity of the diffraction peaks of the H-CL sample, compared with the Nat-CL and Na-CL samples. This result suggests the successful exchange of $H^+$ by $Na^+$ with the treatments by $H_2SO_4$ causing some structural changes and crystallinity loss of the clinoptilolite phase [30].

#### 3.1.2. SEM and EDS

SEM images of natural and modified clinoptilolites show the presence of crystals with forms similar to broad flat rectangular faces with angled corners, this coffin shape is typical of different species of clinoptilolite [31]. Moreover, there was observed no change in the surface or morphological differences with respect to the natural clinoptilolite sample. This confirms the results obtained by XRD analyses.

Chemical composition obtained by EDS show that the sodium content increased two times, whereas it is notably decreased for $K^+$, $Mg^{2+}$, $Ca^{2+}$ and $Al^{3+}$. Acid treatment decrease notably the percentage of exchangeable cation Na, K, Ca and Mg, furthermore a significantly decrease of the aluminum content, and an increase of Si/Al ratio from 4.11 to 7.84 [32]. This ratio is a characteristic tool to determine the hydrophobicity of the zeolitic materials.

#### 3.1.3. Surface area

The results obtained by BET technique show that textural parameters of Nat-CL and Na-CL are similar. However for H-CL, the total pore volume increases approximately 1.5 and 2 times and the surface area increases 4.5 and 5 times in comparison to Na-CL and Nat-CL, respectively. On the other hand, the mean pore diameter decreases 2.5 and 3 times in comparison to Na-CL and Nat-CL. These results indicate that the modification of the Nat-CL with $H_2SO_4$ with 1 M, drastically change the original structure of the zeolitic material.

#### 3.1.4. $pH_{PZC}$

The $pH_{pzc}$ value was found at pH = 8.25 ±0.01 for Nat-CL, while it was 8.00 ± 0.01 and 2.05 ± 0.01 for the Na-CL and H-CL, respectively. This result can be explain by the dealumination phenomenon by the acid treatment of Na-CL which promotes the decrease of the negative charge, consequently diminishes the number of cations and generate a very strong Lewis acid site. Furthermore, an increase of Si/Al was also expected for H-CL [33].

### *3.2. Sorption process*

#### *3.2.1. Kinetics*

Fig. 1 presents the results of kinetic process of Pb(II) sorption with $C_i$ = 10–100 mg/L on Nat-CL, Na-CL and H-CL. As shown in this graph, an increase in initial concentration of Pb(II) in solution (mg/L), increased the amount of ions adsorbed (mg/g). This result can be attributed to higher interaction between metal ions and adsorbent surface [34]. The adsorption capacity of Nat-CL, Na-CL and H-CL increased from 0.945 to 9.583, 0.950 to 10.024, and 0.540 to 1.631 mg/g, respectively when the initial Pb(II) varied from 10 to 100 mg/L. Nevertheless, the efficiency of Pb(II) removal showed the opposite tendency. At higher concentrations, exchangeable sites are saturated, resulting in a decrease in the adsorption capacity [35].

For Nat-CL and Na-CL samples, the time required to achieve the equilibrium sorption capacity ($t_{eq}$) increased with a rise in the initial ions concentration ($t_{eq}$ = 30–180 min, for $C_i(Pb^{2+})$ = 10–40 mg/L and $t_{eq}$ = 240–360 min for $C_i(Pb^{2+})$ = 80–100 mg/L). The initial rapid phase can be attributed to the presence of large number of vacant sites and, as a result there exists, increased the concentration gradient between adsorbate in solution and adsorbate in the adsorbent surface [36,37]. After 180 min, no significant removal was observed, due to the saturation of active sites of the adsorbents by Pb(II) [35].

For higher concentration, the uptake of Pb(II) increased gradually over time from 5 to 360 min and then reaches the equilibrium after 720 min, this can be explained to the decrease in available vacant sites for adsorption.

For H-CL sample, adsorption process generally consisted of two main reaction stages time; initial fast adsorption process from 5 to 360 min, followed by a slow sorption reaction from 360 to 1440 min. At the first stage, about 75%–96% of Pb(II) are sorbed, whereas near of 4%–15% metal amounts are removed during 18 h.

Experimental kinetic data was fitted by the pseudo first order and the pseudo-second-order kinetic models to describe the mechanism involved in the sorption process [38–41]. The linear forms of the pseudo-first order and pseudo-second-order equations are expressed in Eq. (2) and Eq. (3), respectively:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (3)$$

where $q_e$ and $q_t$ (mg/g) are the amounts of Pb(II) adsorbed at equilibrium and at time $t$, respectively, $k_1$ (mg g$^{-1}$ min$^{-1}$) and $k_2$ (mg$^{-1}$ g min$^{-1}$) are the rate constants of pseudo-first and pseudo-second-order sorption, respectively. The values of these parameters are determined from the slope and intercept of the linear plot of $\ln(q_e - q_t)$ *vs.* $t$ (Eq. (2)) and $t/q_t$ *vs.* $t$ (Eq. (3)).

Plotting the experimental data using Eqs. (2) and (3) show that the pseudo-second-order kinetics models give considerably good fit to the data (Table 2). It can see that the values of determination coefficient $R^2$ obtained for the pseudo-second order model are very high. Moreover, the

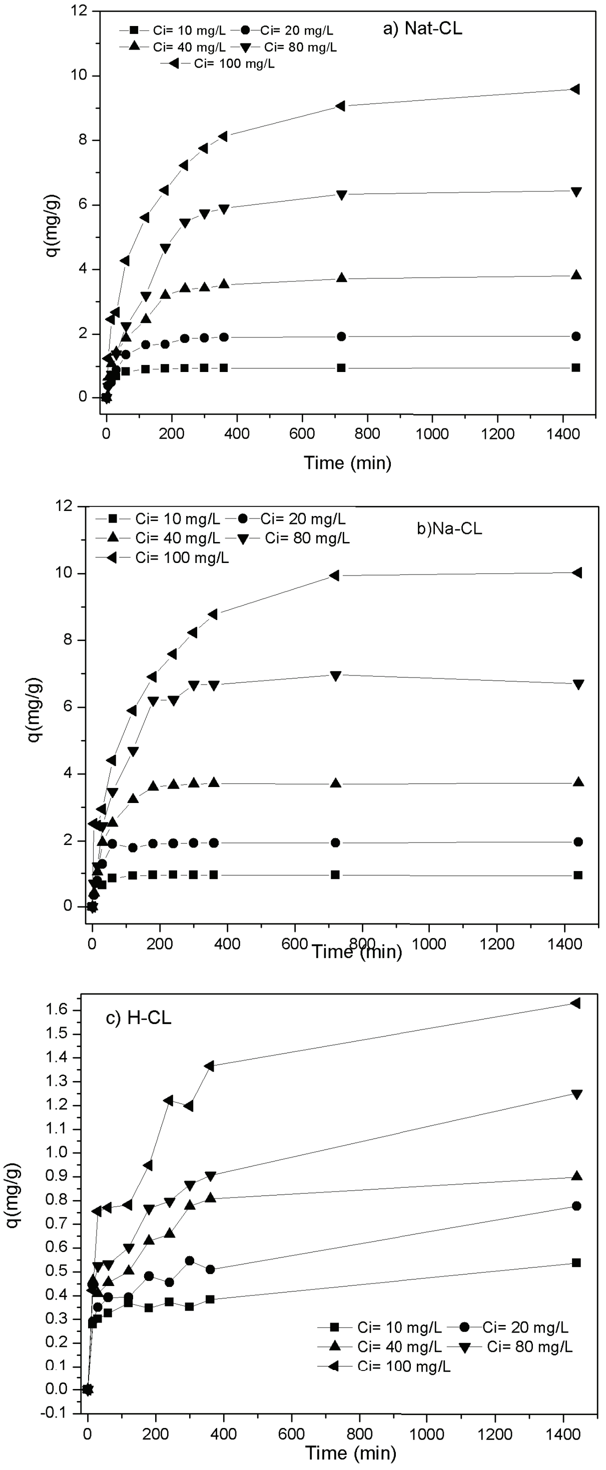

Fig. 1. Adsorption of $Pb^{2+}$ ions as a function of time at different concentrations for (a) Nat-CL, (b) Na-CL and (c) H-CL.

Table 2
Pseudo-second order kinetic model applied to the Pb(II) sorption by natural and modified zeolites

| Concentration of Pb(II) (mg L$^{-1}$) | Zeolitic material | Pseudo-second-order model | | | | |
|---|---|---|---|---|---|---|
| | | $k_2$ ($10^{-2}$) (g m g$^{-1}$ min$^{-1}$) | $q_{e\,\mathrm{calc}}$ (mg g$^{-1}$) | $q_{e\,\mathrm{exp}}$ (mg g$^{-1}$) | $h = k_2q_e^2$ ($10^{-2}$) (mg g$^{-1}$ min$^{-1}$) | $R^2$ |
| 10 | Nat-CL | 15.614 | 0.952 | 0.945 | 5.099 | 0.999 |
| | Na-CL | 19.301 | 0.953 | 0.95 | 17.529 | 0.999 |
| | H-CL | 2.223 | 0.552 | 0.54 | 0.677 | 0.983 |
| 20 | Nat-CL | 1.997 | 1.968 | 1.92 | 7.734 | 0.999 |
| | Na- CL | 4.292 | 1.971 | 1.95 | 7.758 | 0.999 |
| | H- CL | 1.115 | 0.811 | 0.78 | 0.733 | 0.978 |
| 40 | Nat- CL | 0.542 | 3.932 | 3.8 | 8.379 | 0.999 |
| | Na- CL | 1.138 | 3.807 | 3.72 | 16.493 | 0.999 |
| | H- CL | 0.651 | 0.934 | 0.9 | 0.568 | 0.996 |
| 80 | Nat- CL | 0.14 | 7.017 | 6.43 | 6.91 | 0.995 |
| | Na- CL | 0.339 | 7.032 | 6.7 | 16.772 | 0.997 |
| | H- CL | 0.689 | 1.318 | 1.25 | 1.197 | 0.987 |
| 100 | Nat- CL | 0.13 | 10.02 | 9.583 | 13.052 | 0.998 |
| | Na- CL | 0.134 | 10.54 | 10.024 | 14.886 | 0.996 |
| | H- CL | 0.615 | 1.72 | 1.631 | 1.819 | 0.992 |

theoretical $q_{e,\mathrm{cal}}$ values are very closer to the experimental $q_{e,\mathrm{exp}}$ values.

From the results obtained by the pseudo-second-order kinetic model, it can noted that the rate constant ($k_2$) decreases with an increase in initial Pb(II) concentration (Fig. 2). This behavior confirms that at lower concentration, lower competition for the sorption surface sites is obtained. Whereas, for higher concentrations, the competition for the surface active sites is high and, therefore, lower sorption rates are obtained [42,43]. It is important to mention that the parameter *h* is lowest for the Pb(II) sorption by H-CL that shows the structural changes promoted by the acid treatment of the zeolitic material.

### 3.2.2. Isotherms

Langmuir and Freundlich isotherm models are widely used to describe the equilibrium of heavy metals ions between the liquid phase and the solid adsorbent, which determine whether the sorption is of monolayer or multilayer nature, which can be specifically useful to predict the type of adsorption mechanism involved.

Langmuir isotherm model consider that the binding sites are homogeneously distributed over the adsorbent surface and the adsorption takes place at specific homogeneous sites within the adsorbent. This model was evaluated by means of the following equations:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L C_e} \quad (4)$$

where $q_e$ is the amount adsorbed at equilibrium (mg g$^{-1}$); $C_e$ is the equilibrium concentration (mg L$^{-1}$); $K_L$ is the Langmuir constant related to the affinity of the binding site (L mg$^{-1}$) and $q_m$ is the maximum amount of solute adsorbed (mg g$^{-1}$). The coefficients $K_L$ and $q_m$ were determined from the intercept and slope of linear plot of $1/q_e$ vs. $1/C_e$ (Eq. (4)).

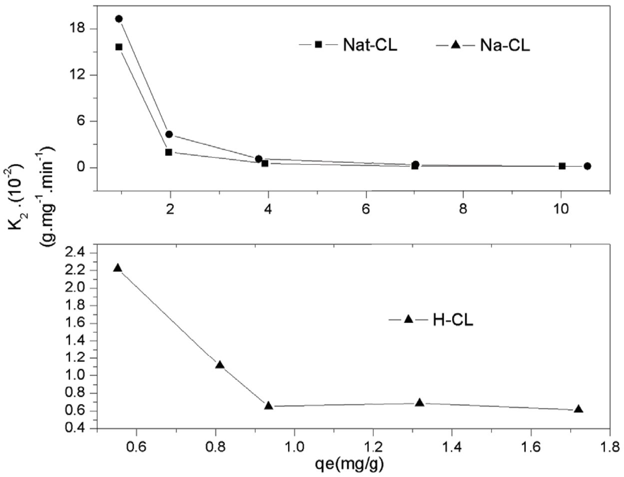

Fig. 2. Pseudo-second order kinetic constant as a function of the equilibrium sorption capacity of Pb$^{2+}$ for Nat-CL, Na-CL and H-CL.

The Freundlich isotherm is commonly used to describe the adsorption for the heterogeneous surface. This isotherm can also be expressed by the following equation (Eq. (5))

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \quad (5)$$

$K_F$ (Lmg$^{-1}$) and *n* are the Freundlich constants that correspond to adsorption intensity and adsorption capacity, respectively. These parameters were obtained from the intercept and slope of linear plot of ln($q_e$) *vs.* ln($C_e$) (Eq. (5)).

The plot of equilibrium concentrations of Pb(II) ions in the solids (Nat-CL, Na-CL and H-CL) and aqueous phases, is presented in Fig. 3. The experimental data were fitted to the linear forms of the Langmuir and Freundlich isotherms as was mentioned before. The values of the corresponding parameters ($K_F$ and $n$) are shown in Table 3. The values of the determination coefficients ($R^2$) of the Freundlich isotherm model are 0.98, which is higher than those obtained for Langmuir model ($0.84 < R^2 < 0.90$), indicating that the experimental data of the Pb(II) sorption by the zeolitic materials can be described by the Freundlich model. Therefore, the Pb(II) sorption by Nat-CL, Na-CL and H-CL is carried out in multilayers. The $n$ values can give an idea about the nature of the interaction between metallic ions and the solid. According to results presented in Table 3, the $n$ values are superior to 1 indicating that the sorption is of a chemical nature. The affinity of Nat-CL, Na-CL and H-CL for Pb(II) is as follows according with the $K_F$ values:

$$K_{\mathrm{FPb\text{-}Na\text{-}CL}} > K_{\mathrm{FPb\text{-}Nat\text{-}CL}} > K_{\mathrm{FPb\text{-}H\text{-}CL}}$$

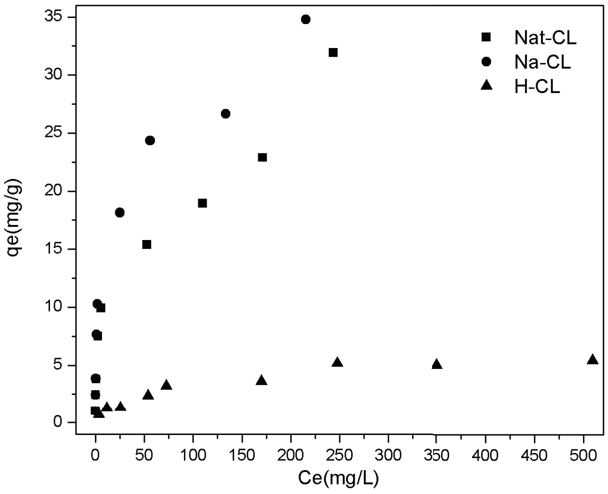

Fig. 3. Pb(II) sorption isotherms for Nat-CL, Na-CL and H-CL.

Table 3
Parameters obtained from Langmuir and Freundlich models that describe the sorption of $Pb^{2+}$ by Nat-CL, Na-CL and H-CL

| Zeolitic material | Isotherm models | | | | | |
|---|---|---|---|---|---|---|
| | Langmuir | | | Freundlich | | |
| | $K_L$ (L mg$^{-1}$) | $q_m$ (mg g$^{-1}$) | $R^2$ | $K_F$ (mg g$^{-1}$) (L mg$^{-1}$)$^{1/n}$ | $n$ | $R^2$ |
| Nat -CL | 68.5 | 7.30 | 0.84 | 4.95 | 3.47 | 0.98 |
| Na -CL | 12.40 | 9.06 | 0.90 | 6.10 | 2.93 | 0.98 |
| H -CL | 0.066 | 3.47 | 0.89 | 0.40 | 2.30 | 0.97 |

The high affinity of Na-CL for Pb(II) compared with Nat-CL can be attributed to the high mobility of $Na^+$ ions in Na-CL, which improves the ion exchange according with the following reaction:

$$\mathrm{Na\text{-}CL}_{(z)} + \mathrm{Pb}^{2+}_{(s)} \leftrightarrow \mathrm{Pb\text{-}CL}_{(z)} + 2\mathrm{Na}^{+}_{(s)}$$

where $z$ represents the zeolitic material and $s$ the aqueous solution.

According to the Langmuir model, it is clear that the maximum adsorption capacity of the H-CL is 2.6 and 2.1 times lower than Na-CL and Nat-CL, respectively. The constant related to the affinity of the binding site ($K_L$) is lowest for H-CL, and this result is important if it is considered the recovery of the Pb(II) from the H-CL. Therefore, in the Pb(II) sorption process, the specific surface area of the zeolitic materials is not a parameter to play an important role.

### *3.2.3. Influence of adsorbent dosage*

Fig. 4 depicts the percentage lead removal as a function of time with different initial amounts of Nat-CL, Na-CL and H-CL (from 0.1 to 1 g). It can be observed that for all zeolitic materials, the percentage removal of lead increased with increasing mass of the zeolitic materials. This finding is due to the presence of more availability of the exchangeable sites at higher amount of the adsorbent [44].

As shown in Fig. 4, it can noted that 0.5 g of Nat-CL and 0.4 of Na-CL, were sufficient to remove over 100% of Pb(II) within the first 30 min and further addition of the adsorbent beyond this did not cause any significant change in the adsorption. Whereas, for H-CL zeolite, it can observed that the percentage of metal uptake increase from 30% with 0.1 g up to 95% approximately with 1.0 g for 360 min. In this case, various investigations reported that at high zeolite dose, the competition between ion metals is reduced due to the availability of more sorption site [45].

The experimental data were adjusted to pseudo second-order kinetic model obtaining a determination coefficient > 0.99. Fig. 5 shows the plots of $t/q$ versus $t$ of Nat-CL, Na-CL and H-CL. The variation of kinetic rate constant $k_2$ (g mg$^{-1}$ min$^{-1}$) as a function of the adsorbent mass presents an exponential behavior for Nat-CL and Na-CL, whereas for H-CL, $k_2$ increase linearly with amount of adsorbent. This result confirms that the pseudo-second-order kinetic constant depends not only of the sorbent dosage but also of the modification of the zeolitic material.

### *3.2.4. Influence of pH*

The percentage of adsorption of metal ions largely depends to the initial pH of aqueous solution, due to its impact on the surface adsorption sites and on the speciation of metal ions at different pHs [46].

The influence of pH on the sorption of the Pb(II) by Nat-CL, Na-CL and H-CL is shown in Fig. 6. This figure illustrates the percentage of metal removal as a function of time at different initial pH values. It is important to take account the surface charge of the zeolitic materials that can play a role in the sorption process as was mentioned above.

For Nat-CL and Na-CL samples (Fig. 6(a) and 6(b)), it can be observed that when the initial pH of the solution

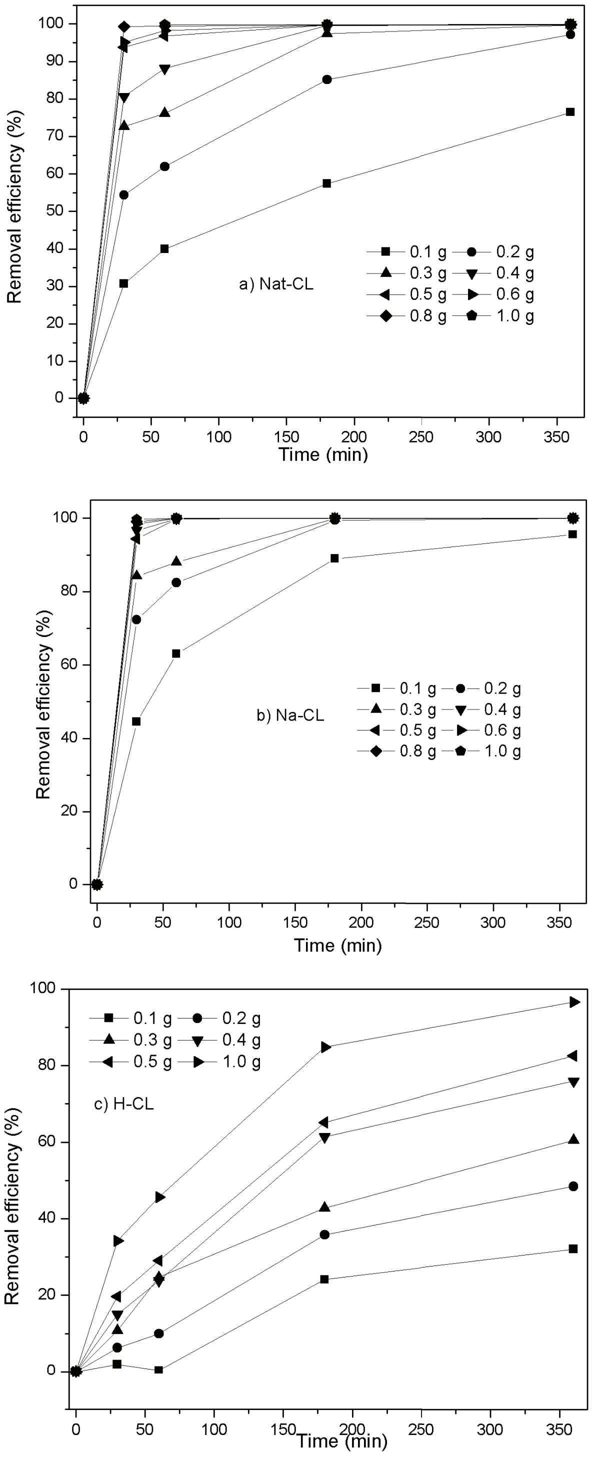

Fig. 4. Effect of the (a) Nat-CL, (b) Na-CL and (c) H-CL dosage on the Pb(II) sorption as a function of time, considering T = 25°C, pH = 2, $C_iPb^{2+}$ = 100 mg/L.

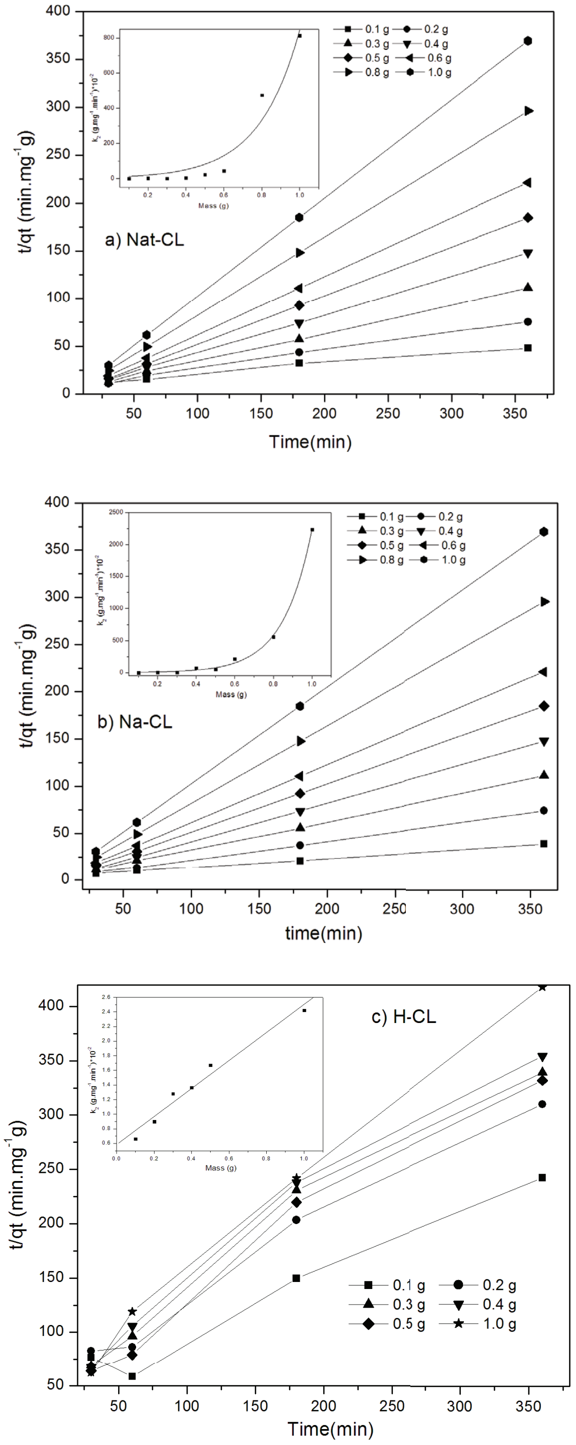

Fig. 5. Pseudo second order kinetic model applied to the Pb(II) sorption by (a) Nat-CL, (b) Na-CL and (c) H-CL, with different zeolitic material mass. The inside curves represent $k_2$ *vs.* mass.

is ≥ 3.0, approximately 100% of Pb(II) uptake is achieved within the first 15 min, whereas when initial pH = 2, a gradual increase in the removal of Pb(II) was recorded up to 720 min for Nat-CL and Na-CL. These results indicate that the sorption of Pb(II) by these zeolitic materials could be involved two mechanism: (a) ion exchange when pH ≤ 2 and (b) precipitation on the surface and ion exchange for initial pH ≥ 3 [34, 46].

As show in Fig. 6(c), the removal extent of Pb(II) increased from 10% (pH = 2) to 85% (pH = 6). The $pH_{pzc}$

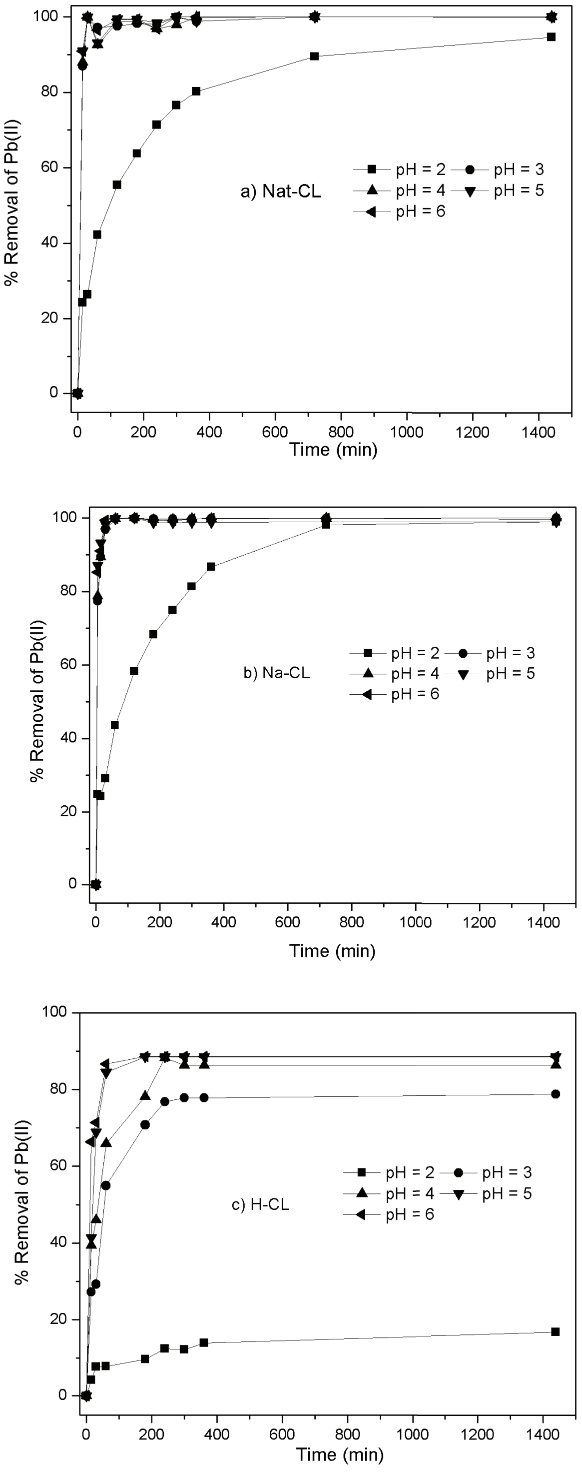

Fig. 6. Influence of pH on the sorption of Pb(II) by (a) Nat-CL, (b) Na-CL and (c) H-CL.

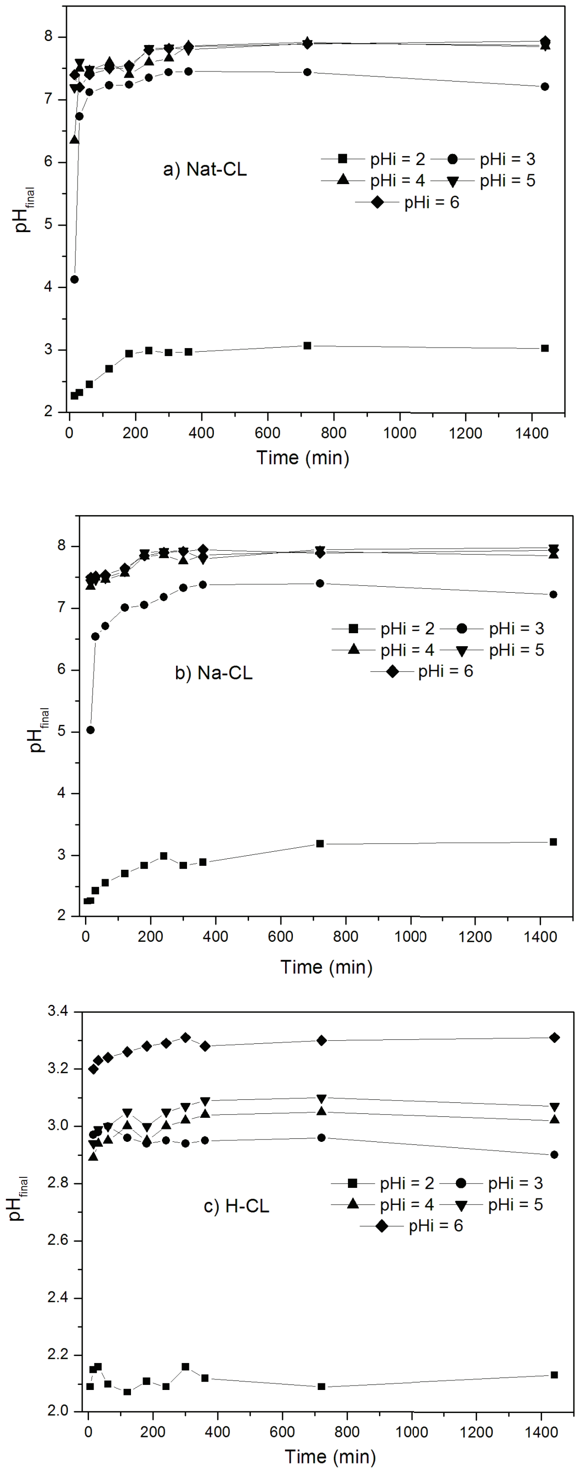

Fig. 7. Variation of final pH of the solutions after the Pb(II) sorption by (a) Nat-CL, (b) Na-CL and (c) H-CL.

of H-CL was 2.05 ± 0.01, at pH = 2, the surface of H-CL became positively charged and the removal of Pb(II) is less due to the $H^+$ competes with metal ions for the adsorption sites. However, with the increasing pH, the surface of H-CL become more negatively charged and the repulsive force decrease and therefore the removal of Pb(II) begins to increase [46].

In order to confirm this hypothesis, the pH of the solution after each contact time was measured. Fig. 7(a) and 7(b) show the results obtained. It is evident from this figure

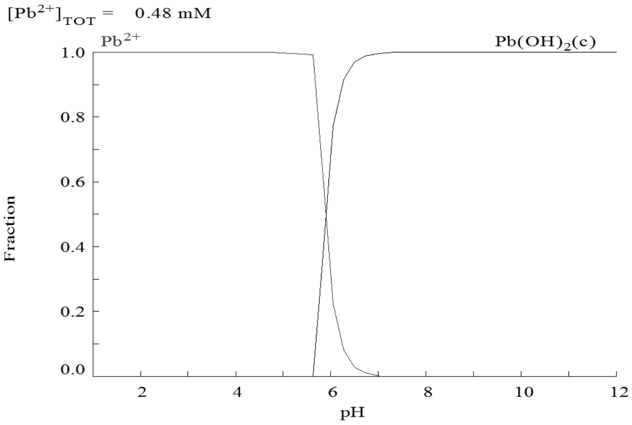

Fig. 8. Speciation diagram of Pb as a function of pH values.

that when initial pH ≥ 3, the final pH of aqueous solution reached values from 6 to 8 approximately, this indicate that the metallic solutions were basified by Nat-CL and Na-CL after the sorption processes. In this pH region, several studies has been reported the substantial increase in the sorption of metal ions on surface due to the possible precipitation of metal ions with their hydroxide form as white $Pb(OH)_2$ solid [46–49].

Fig. 7(c) shows that when initial pH = 2–6, the final pH of aqueous solutions after each contact time vary between 2 and 3. In this pH region predominate the $Pb^{2+}$ ions and suggest that the removal of Pb(II) by H-CL was carried out by ion exchange process.

Fig. 8 presents the Pb speciation diagram as a function of pH in aqueous solution. In this graph it can be observed that when pH ≤ 6, $Pb^{2+}$ ions are predominant. However, at pH values between 5 and 8, the hydroxide species are generated.

## 4. Conclusions

From this work, it is concluded that the crystalline structure of natural clinoptilolite (Nat-CL) was not affected by sodium and acid treatments. However, chemical composition of natural zeolite changes after contact of Nat-CL with NaCl and $H_2SO_4$ solutions. The acid treatments of the Nat-CL promote the dealuminization of the material increasing the Si/Al ratio. The $pH_{pzc}$ is similar between Nat-CL and Na-CL ($pH_{pzc} = 8$) and it is drastically different for H-CL ($pH_{pzc} = 2$).

The pseudo-second-order kinetic model best describes the sorption behavior and the $k_2$ values depends of (a) the initial concentration of the Pb(II) in solution, (b) the zeolitic material dosage and (c) its modification.

The experimental data of the isotherms well fitted to the Freundlich isotherm model. The $K_F$ parameter is higher for Na-CL than Nat-CL and H-CL. The maximum Pb(II) adsorption capacity ($q_m$) is highest for Na-CL (9.06 mg/g).

The sorption of Pb(II) by Nat-CL and Na-CL could be involved two mechanism: (a) ion exchange when pH ≤ 2 and (b) precipitation on the surface for initial pH ≥ 3. In the case of H-CL, only an ion exchange could be possible.

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## References

[1] L. Selwyn, Health and safety concerns relating to lead and lead compounds in conservation, J. Can. Assoc. Conserv., 30 (2005) 18–37.
[2] J. Goel, K. Kadirvelu, C. Rajagopal, V.K. Garg, Removal of lead (II) by adsorption using treated granular activated carbon: Batch and column studies, J. Hazard. Mater., B125 (2005) 211–220.
[3] H. Ucun, Y.K. Bayhan, Y. Kaya, A. Cakici, O.F. Algur, Biosorption of lead (II) from aqueous solution by cone biomass of Pinus sylvestris, Desalination, 154 (2003) 233–238.
[4] G. Chen, Electrochemical technologies in wastewater treatment, Sep. Purif. Technol., 38 (2004) 11–41.
[5] M.A. Barakat, New trends in removing heavy metals from industrial waste water, Arabian J. Chem., 4 (2011) 361–377.
[6] E.H. Ali, M. Hashem, Removal efficiency of the heavy metals Zn(II), Pb(II) and Cd(II) by Saprolegnia delica and Trichoderma viride at different pH values and temperature degrees, Mycobiology, 35 (2007)135–144.
[7] F. Fu, Q. Wang, Removal of heavy metal ions from wastewaters: a review, J. Environ. Manage., 92 (2011) 407–418.
[8] A. Zendelska, M. Golomeova, K. Blazev, B. Krstev, B. Golomeov, A. Krstev, Adsorption of copper ions from aqueous solutions on natural zeolite, Environ. Prot. Eng., 41 (2015) 18–36.
[9] S.M. Shaheen, A.S. Derbalah, F.S. Moghanm, Removal of heavy metals from aqueous solution by zeolite in competitive sorption system, Int. J. Environ. Sci. Develop., 3 (2012) 362–367.
[10] R. Egashira, S. Tanabe, H. Habaki, Adsorption of heavy metals in mine wastewater by Mongolian natural zeolite, Procedia Eng., 42 ( 2012 ) 49–57.
[11] L. Mihaly-Cozmuta, A. Mihaly-Cozmuta, A. Peter, C. Nicula, H. Tutu, D. Silipas, E. Indrea, Adsorption of heavy metal cations by Na-clinoptilolite: Equilibrium and selectivity studies, J. Environ. Manage., 137 (2014) 69–80.
[12] S.S.H. Ghahfarokhi, A. Landi, H. Khademi, S. Hojati, Removal of $Cd^{2+}$ and $Pb^{2+}$ ions from aqueous solutions using Iranian natural zeolite and sepiolite, J. Environ. Stud., 40 (2014) 189–198.
[13] V.J. Inglezakis, M.A. Stylianou, D. Gkantzou, M.D. Loizidou, Removal of Pb(II) from aqueous solutions by using clinoptilolite and bentonite as adsorbents, Desalination, 210 (2007) 248–256.
[14] S. Wang, Y. Peng, Natural zeolites as effective adsorbents in water and wastewater treatment, Chem. Eng. J., 156 (2010) 11–24.
[15] J. Lin, Y. Zhan, Z. Zhu, Adsorption characteristics of copper (II) ions from aqueous solution onto humic acid-immobilized surfactant-modified zeolite, Colloid Surface A, 384 (2011) 9–16.
[16] M.M. Hussein, K.M. Khader, S.M. Musleh, Characterization of raw zeolite and surfactant-modified zeolite and their use in removal of selected organic pollutants from water, Int. J. Chem. Sci., 12 (2014) 815–844.
[17] M. Sakizci, L.O. Tanriverdi, Influence of acid and heavy metal cation exchange treatments on methane adsorption properties of mordenite, Turk. J. Chem., 39 (2015) 970–983.
[18] B.R. Putra, L.K. Darusman, E. Rohaeti, Carbon paste electrode hexadecyltrimethylammonium bromide modified natural zeolite for chromium(VI) detection, Indo. J. Chem., 13 (2013) 122–128.
[19] L.E. Burris, M.C.G. Juenger, The effect of acid treatment on the reactivity of natural zeolites used as supplementary cementitious materials, Cement Concrete Res., 79 (2016) 185–193.
[20] M. Panayotova, B. Velikov, Influence of zeolite transformation in a homoionic form on the removal of some heavy metal ions from wastewater, J. Environ. Sci. Heal A., 38 (2003) 545–554.

[21] V.J. Inglezakis, C.D. Papadeus, M.D. Loizidou, H.P. Grigoropoulou, Effects of pretreatment on physical and ion exchange properties of natural clinoptilolite, Environ. Technol., 22 (2001) 75–82.

[22] S.K. Ouki, C. Cheeseman, R. Perry, Effects of conditioning and treatment of chabazite and clinoptilolite prior to lead and cadmium removal, Environ. Sci. Technol., 27 (1993) 1108–1116.

[23] M.A.A. Zaini, R. Okayama, M. Machida, Adsorption of aqueous metal ions on cattle-manure-compost based activated carbons, J. Hazard. Mater., 170 (2009) 1119–1124.

[24] C.X. Rojas-Pavón, M.T. Olguín, M.J. Jiménez-Cedillo, A.M. Maubert, Sorption properties of modified clinoptilolite-and mordenite-rich tuffs for manganese removal from aqueous systems, Res. Rev. Mater. Sci. Chem., 5 (2015) 29–61.

[25] P.C.C. Faria, J.J.M. Órfão, M.F.R. Pereira, Adsorption of anionic and cationic dyes on activated carbons with different surface chemistries, Water Res., 38 (2004) 2043–2052.

[26] R.W. Puls, R.M. Powell, D. Clark, C.J. Eldred, Effects of pH, solid/solution ratio, ionic strength, and organic acids on Pb and Cd sorption on kaolinite, Water, Air, Soil Poll., 57–58 (1991) 423–430.

[27] M. Saleem, R. Qadeer, J. Hanif, M. Afzal, Effect of pH on the adsorption of $Ce^{3+}$ $Sm^{3+}$ $Eu^{3+}$ and $Gd^{3+}$ ions on activated charcoal, J. Radioanal Nucl. Ch., 182 (1994) 415–419.

[28] V.K. Jha, S. Hayashi, Modification on natural clinoptilolite zeolite for its $NH^{4+}$ retention capacity, J. Hazard. Mater., 169 (2009) 29–35.

[29] A. Nezamzadeh-Ejhieh, S. Moeinirad, Heterogeneous photocatalytic degradation of furfural using NiS-clinoptilolite zeolite, Desalination, 273 (2011) 248–257.

[30] C. Cobzaru, S. Oprea, E. Dumitriu, V. Hulea, Gas phase aldol condensation of lower aldehydes over clinoptilolite rich natural zeolites, Appl. Catal. A-Gen., 351 (2008) 253–258.

[31] V.J. Inglezakis, A.A. Zorpas, Natural zeolites structure and porisity, Handbook of Natural Zeolites (2012): pp. 133–147.

[32] R.M. Barrer, M. Makki, Molecular sieve sorbents from clinoptilolite, Can. J. Chem., 42 (1961) 1481–1487.

[33] M.P. Elizalde-González, J. Mattusch, R. Wennrich, P. Morgenstern, Uptake of arsenite and arsenate by clinoptilolite richtuffs, Micropor. Mesopor. Mat., 46 (2001) 277–286.

[34] M. Borandegi, A. Nezamzadeh-Ejhieh, Enhanced removal efficiency of clinoptilolite nano-particles toward Co(II) from aqueous solution by modification with glutamic acid, Colloid Surface A, 479 (2015) 35–45.

[35] A. Naghash, A. Nezamzadeh-Ejhieh, Comparison of the efficiency of modified clinoptilolite with HDTMA and HDP surfactants for the removal of phosphate in aqueous solutions, J. Ind. Eng. Chem., 31 (2015) 185–191.

[36] Q. Du, S. Liu, Z. Cao, Y. Wang, Ammonia removal from aqueous solution using natural Chinese clinoptilolite, Sep. Purif. Technol., 44 (2005) 229–234.

[37] S.S. Kalalagh, H. Babazadeh, A.H. Nazemi, M. Manshouri, Isotherm and kinetic studies on adsorption of Pb, Zn and Cu by kaolinite, Caspian J. Env. Sci., 9 (2011) 243–255.

[38] W.W.S. Ngah, L.C. Teong, R.H. Toh, M.A.K.M. Hanafiah, Utilization of chitosan-zeolite composite in the removal of Cu(II) from aqueous solution: adsorption, desorption and fixed bed column studies, Chem. Eng. J., 209 (2012) 46–53.

[39] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, Process Biochem., 34 (1999) 451–465.

[40] M. Arshadi, M.J. Amiri, S. Mousavi, Kinetic, equilibrium and thermodynamic investigations of Ni(II), Cd(II), Cu(II) and Co(II) adsorption on barley straw ash, Water Resour. Ind., 6 (2014) 1–17.

[41] Y.S. Ho, G. McKay, D.A.J. Wase, C.F. Foster, Study of the sorption of divalent metal on to peat, Adsorpt. Sci. Technol., 18 (2000) 639–650.

[42] W.A. Carvalho, C. Vignado, J. Fontana, M.B. Riboldi, The removal of heavy metal ions from aqueous effluents by modified clays: Retention of Cd(II) and Ni(II)Ions, Adsorpt. Sci. Technol., 25 (2007) 673–692.

[43] A. Gunay, E. Arslankaya, I. Tosun, Lead removal from aqueous solution by natural and pretreated clinoptilolite: adsorption equilibrium and kinetics, J. Hazard. Mater., 146 (2007) 362–371.

[44] D.N. Tumin, L.A. Chuah, Z. Zawani, A.S. Rashid, Adsorption of copper from aqueous solution by elais guineensis kernel activated carbon, J. Eng. Sci. Technol., 3 (2008) 180–189.

[45] T.K. Naiya, A.K. Bhattacharya, S.K. Das, Clarified sludge (basic oxygen furnace sludge)-an adsorbent for removal of Pb(II) from aqueous solutions-kinetics, thermodynamics and desorption studies, J. Hazard. Mater., 170 (2009) 252–262.

[46] M. Anari-Anaraki, A. Nezamzadeh-Ejhieh, Modification of an Iranian clinoptilolite nano-particles by hexadecyltrimethyl ammonium cationic surfactant and dithizone for removal of Pb(II) from aqueous solution, J. Colloid Interf. Sci., 440 (2015) 272–281.

[47] A.H. Oren, A. Kaya, Factors affecting adsorption characteristics of $Zn^{2+}$ on two natural zeolites, J. Hazard. Mater., B131 (2006) 59–65.

[48] A. Benhammou, A. Yaacoubi, L. Nibou, B. Tanouti, Adsorption of metal ions onto Moroccan stevensite: kinetic and isotherm studies, J. Colloid Interf. Sci., 282 (2005) 320–326.

[49] W.W.S. Ngah, L.C. Teong, M.A.K.M. Hanafiah, Adsorption of dyes and heavy metal ions by chitosan composites: a review, Carbohyd. Polym., 83 (2011) 1446–1456.