

Use of natural and modified zeolites from Bulgarian and Chilean deposits to improve adsorption of heavy metals from aqueous solutions

Nikolay Popov, Todorka Popova, Jorge Rubio, Silvio Roberto Taffarel

Abstract. The present work aims at characterization of natural zeolites and their adsorption properties in respect to Pb^{+2} , Cd^{+2} , Fe^{+2} and Mn^{+2} ions in aqueous solutions. The zeolitized tuff samples provided from the Bulgarian deposits Belia Bair (BB) and Beli Plast (BP) and from Northern Chile (NCl), were studied in respect to chemical and mineralogical composition, as well as adsorption and ion exchange properties. The average content of clinoptilolite for both Bulgarian samples was found to be more than 75% and they had ion exchange capacity (NH_4^+) varying from 107 to 121 meq/100g, respectively. Thermo-chemical modification of natural clinoptilolite from BB and BP was made in order to increase the ion exchange capacity up to 180 meq/100g. The results showed almost complete removal (>90 %) of all the metal ions studied. Activations of NCl-zeolite ($118 m^2 g^{-1}$) by pre-treatment with various ions greatly enhanced the Mn adsorption and mechanisms involved were elucidated. The maximum adsorption capacity (pH=6) was decreasing for activation with NaCl ($0.77 meq Mn^{2+} g^{-1}$), NaOH ($0.76 meq Mn^{2+} g^{-1}$), Na_2CO_3 ($0.72 meq Mn^{2+} g^{-1}$), NH_4Cl ($0.67 meq Mn^{2+} g^{-1}$) compared to the natural ($0.26 meq Mn^{2+} g^{-1}$). The used Langmuir isotherm model showed excellent correlation with the equilibrium data and the maximum capacity to adsorption depended on the activation type, realized before the adsorption experiments. The treatment of the heavy metals bearing solutions using filter packets and stirred flasks was studied experimentally. The filters were made by a special technology, following the standard requirements in Bulgaria, i.e. particle size distribution, mass ratio (g/m^2) and permeability. These filters purified the waters substantially lowering the metal ion concentrations well below sanitary standard limits. The reduction of Pb^{2+} was about 18 times, Mn^{+2} – more than 20 times, and Fe^{+2} and Cd^{+2} – more than 50 times. The total reduction of the heavy metals in solutions was more than 25 times and varied within the limits of 5 to 14 mg/l after the third stage of treatment. Best results were obtained with blends of BB and BP natural clinoptilolite at 50:50 ratios and after the thermo-chemical treatment.

Key words: clinoptilolite, ion exchange, heavy metals

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Николай Попов, Тодорка Попова, Хорхе Рубио, Силвио Роберто Тафарел. Използване на природни и модифицирани зеолити от български и чилийски находища за адсорбция на тежки метали от водни разтвори

Резюме. Настоящата работа представя характеристиката на природни зеолити и резултатите от адсорбцията на Pb^{2+} , Cd^{2+} , Fe^{2+} и Mn^{2+} от водни разтвори. Пробите от зеолитизирани туфи са от

българските находища Белия баир (ВВ) и Бели Пласт (ВР), както и от северната част на Чили (NCL). Пробите са охарактеризирани по отношение на химически и минерален състав, адсорбционни и йонообменни свойства и рентгенов анализ. Установено е, че средното съдържание на клиноптилолит в българските проби е повече от 75% и те са с йонообмен капацитет (СЕС) по NH_4^+ в рамките на 107–121 meq/100g. Проведена е термохимична активация на пробите от ВВ и ВР с цел да се увеличи обменния капацитет до 180 meq/100 g. Резултатите от адсорбцията на комплекса от метални катиони показват почти пълно отстраняване ($> 90\%$) на всички от изследваните метални йони. Активацията на NCL-зеолит ($118 \text{ m}^2/\text{g}$) след предварителната обработка с различни йони показва значително увеличение на адсорбцията на Mn като е изяснен и нейния механизъм. Максималният капацитет на мангановата адсорбция е при $\text{pH}=6$ и тя намалява при активиране с NaCl ($0,77 \text{ meq Mn}^{2+}/\text{g}$), с NaOH ($0,76 \text{ meq Mn}^{2+}/\text{g}$), с Na_2CO_3 ($0,72 \text{ meq Mn}^{2+}/\text{g}$), с NH_4Cl ($0,67 \text{ meq Mn}^{2+}/\text{g}$), докато при изходните зеолити е $0,26 \text{ meq Mn}^{2+}/\text{g}$). Моделът на Langmuir–изотермата показва отлична корелация с равновесните данни. Максималният капацитет на мангановата адсорбция зависи от типа на активирането, осъществен преди адсорбцията. Експерименталното пречистване на водите от тежките метали е проведено с помощта на филтър–пакети. Филтрите са направени по специална технология, съгласно стандартните изисквания в България, т.е. съобразен е с размера на частиците и разпределението им във филтъра, съотношението на масата (g/m^2) и пропускливостта на слоя. Тези филтри пречистват водите до концентрация на метални йони под санитарните стандартни граници. Намаляването на Pb^{2+} е около 18 пъти, на Mn^{2+} – повече от 20 пъти и Fe^{2+} и Cd^{2+} – над 50 пъти. Общото намаление на тежките метали е повече от 25 пъти и варира в границите от 5 до 14 mg/l след третия етап на пречистване. Най-добри резултати са получени със смеси от ВВ и ВР природен клиноптилолит в съотношение 50:50 и след термохимичната им обработка.

Introduction

Many toxic heavy metals have been discharged into the environment as industrial waste causing serious soil and water pollution. Ions like Pb^{+2} , Cd^{+2} , Fe^{+2} and Mn^{+2} are especially common metals that tend to accumulate in organisms, causing numerous diseases and disorders (Inglezakis et al. 2002). Manganese exists in water but may also be present due to underground pollution sources. Manganese may become noticeable in tap water at concentrations higher than 0.05 mg/l of water by imparting a color, odor, or taste to the water. According to the Division of Environmental Epidemiology and Occupational Health of Connecticut, health effects from Mn are not a concern until concentrations are approximately 10 times higher. The levels of Mn in groundwater from natural leaching processes can vary widely, depending upon the types of rock and minerals present at the water table. Typically, Mn concentrations from natural processes are low but can range up to 1.50 mg/l or higher. Sources of pollution, rich in organic matter (e.g., runoff from landfills, composts, brush or silage piles, or chemicals such as

gasoline), can add to the background level by increasing Mn release from soil or bedrock into groundwater.

Several treatment technologies, such as chemical precipitation, ultra filtration, adsorption, were applied. Wastewaters released by mining, mineral processing and smelting enterprises are heavily polluted with these cations that are classified as hazardous pollutants. Numerous processes exist for removing dissolved heavy metals, including ion exchange, precipitation, phytoextraction, ultrafiltration, reverse osmosis, and electro dialysis (Erdem et al. 2004). The use of alternative low-cost materials as potential sorbents for the removal of heavy metals has been emphasized recently. Zeolites represent an attractive native material for removing heavy metal ions from industrial and processing effluent water. Their advantages are the following: low cost, stability and abrasion resistance, low swelling capacity, their exchangeable ions are relatively harmless Na, Ca and K; no secondary pollution can be caused during zeolites preparation and use, and relatively easy regeneration of spent zeolites.

Many authors studied the use of zeolites as such (natural) in environmental applications mainly to remove ions from wastewater by adsorption ionic exchange processes (Inglezakis et al. 2002; Ruthven 2001; Doula & Ioannou 2003). Investigations showed that there is a significant increase in pollutants uptake when natural zeolites are pre-treated with aqueous solutions containing sodium cations (activation stage), which improve materials reactivity (Oliveira & Rubio 2007).

As seen from the literature review, zeolites can be used for the removal of some heavy metals from wastewaters. The clinoptilolite samples from different regions show different behavior in ion-exchange processes. In this study, the adsorption properties of natural and modified zeolite (South-East Bulgaria and Northern Chile, respectively) with respect to some heavy metals cations in solution were investigated.

Experimental

Materials and reagents

The samples were taken from Belia Bair (designated here as BB-zeolite) and Beli Plast (BP-zeolite) zeolitized tuffs deposits. The open pit mines are placed near to Kardzhali town in Eastern Rhodopes Mountain, Bulgaria. The samples were crushed in a jaw and rotary crushers up to 10 mm. The crushed samples were homogenized and passed through 0.8×1.25 mm sieves. Representative samples of 10 kg from BB- and BP-zeolite (fraction 0.8–1.25 mm) were dried in an oven at 100±5°C for 24 h before characterization and experimentation (Popov et al., 1992).

Inorganic chemicals were supplied by Merck as analytical-grade reagents. The metal ions studied were Fe²⁺, Mn²⁺, Pb²⁺, and Cd²⁺. The synthetic stock solution (total cation concentration, 1000 mg/l) of these metals were prepared using their salts FeSO₄·H₂O, MnSO₄·H₂O, Pb(CH₃COO)₂·3H₂O and CdJ₂, respectively.

Analytical purity sodium carbonate and

calcium hydroxide were used for determination of static ion-exchange ability. Analytical purity hydrochloric acid and sodium bicarbonate were used to treat the BB- and BP-zeolites and to modify the materials (functionalization) with Na⁺ ions in the adsorption studies. All solutions were prepared with deionised water.

NCl-zeolite (Northern Chile) granulated sorbent from the Minera Formas® Company with grain size of about 3 mm was prepared and used in the adsorption studies. It consists mainly of clinoptilolite (Oliveira & Rubio 2007).

Synthetic ammonia solutions were prepared with NH₄Cl (Merck TM analytical purity) for the determination of the cation-exchange capacity of the NCl-zeolite. Analytical purity MnCl₂·4H₂O (Synth®) was used in the preparation of Mn synthetic solutions for the adsorption study. HNO₃ and KOH solutions were used for pH adjustment. Ultra purity (> 99.999%) nitrogen gas from Air Products® was used for specific surface area determination of the NCl-zeolite (by nitrogen adsorption method).

Solutions of 1M of NaCl (Synth®), NH₄Cl (Merck TM), Na₂CO₃ (MerckTM) and NaOH were used for NCl-zeolite activation. All solutions were prepared using deionised water. All studies were performed in duplicate.

Manganese concentration was determined using atomic absorption spectroscopy (Spectr AA 110, Varian®). The results are expressed in mg Mn l⁻¹. Ammonia concentration was determined using a titrimetric method, with preliminary distillation step, based on the Standard Methods for the Examination of Water and Wastewater (APHA 1995). Results are expressed in mg NH₃-N l⁻¹. The solutions pH was determined using a Model AM 608, ANALION®.

Methods

Zeolites characterization

The chemical and mineralogical composition and physical properties of the Bulgarian

zeolitized tuffs deposits were described in Rainov et al. (1997 and references therein). Chemical composition of the zeolite samples was determined by the usual analytical methods for silicate materials. The concentration of mineral phases was evaluated by semiquantitative X-ray diffraction analysis on a D-500 Siemens diffractometer, according to the method of Peter & Kalman (1964).

The cation-exchange capacity (CEC) of the BB- and BP-zeolites was determined according to the method of Ming et al. (1993) and the ion-exchange properties were studied using the method of Chapman (1965).

Electron microscopy study and ion-exchange tests were performed. Scanning electron microscopy (Jeol Superprobe 733 at the Geological Institute of BAS) was used for photomicrographs. The static ion-exchange ability of natural and Na and Ca enriched forms of the studied samples were determined using the method of Chapman (1965). The modification of the natural BB- and BP-zeolite was performed contacting the samples with an aqueous solution of sodium carbonate and calcium hydroxide.

The particle size distribution of the NCl-zeolite was determined using laser diffraction equipment (CILAS® 1064) and the specific surface area was evaluated by the nitrogen gas adsorption method, using automated equipment (Autosorb 1 – Quantachrome Instruments TM), employing multipoint BET isotherm adsorption data fitting.

Suspensions (0.01% v/v) of the NCl-zeolite, previously sieved below 37 µm (400 Mesh Tyler TM), in a 10⁻³ mol/l solution of KNO₃ were used and the medium pH was controlled with the addition of HNO₃ (pH<7) and KOH (pH>7), separately.

Pre-treatment, modification and adsorption studies

Chemical and thermo-chemical modifications of natural clinoptilolites from BB and BP samples were made in order to increase the ion-exchange capacity. The chemical modification

included: pre-treatment of the zeolites performed by contacting the material with 0.1 N HCl solution during 48 h at room temperature. The modification of the pre-treated adsorbents was carried out contacting the activated zeolite sample with 7.5% NaHCO₃ solution during 24 h in drum activator (volume 12 l and revolutions 45 /min⁻¹). Then, the modified zeolite was washed three times and used in the adsorption studies.

The thermo-chemical modification included temperature treatment of the zeolites at 250°C during 24 h and then 8 h keeping at room temperature. The modification of the thermo-treated adsorbents was carried out contacting the activated zeolite with 7.5% NaHCO₃ solution during 24 h in drum activator (volume 12 l and revolutions 45/ min⁻¹). Then, the modified zeolite was washed 3 times and used in the adsorption studies.

Adsorption experiments were carried out in 1 l filter packet glass columns with run-off tap. The filter packet columns are presented on Figure 1. Each column contains 1 kg filter packet of the studied mixture from BB- and

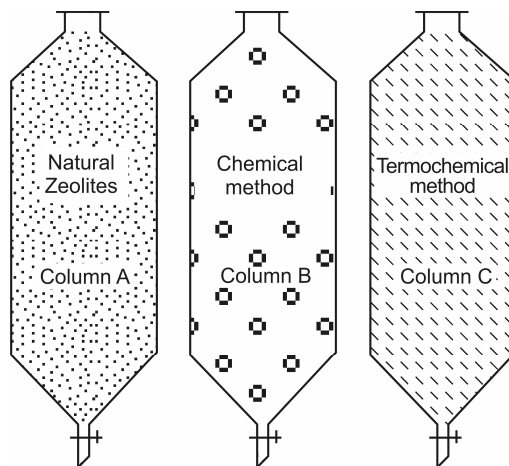


Fig. 1. Filter packet columns for adsorption study. (column A, natural zeolite; column B, chemical modified zeolite; column C, thermo-chemical modified zeolite)

BP-zeolite in ratio 50:50. Column A contains natural zeolite, column B – chemical modified zeolite and column C – thermo-chemically modified zeolite. The laboratory experiments were conducted with 1000 ml of solutions containing heavy metal ions of Pb, Cd, Fe, Mn with desired concentrations. The solution flowed through the columns at a rate of 8 l/h. The experiments were carried out at different stage treatment:

- The aqueous solution of heavy metal ions passes through column A.
- The aqueous solution of heavy metal ions passes through column A and column B continuously.
- The aqueous solution of heavy metal ions passes through column A and column C continuously.
- The aqueous solution of heavy metal ions passes through column A, column B and column C continuously.

The NCl-zeolite activation was made through the contact between zeolite with 1M solutions of NaCl, NH₄Cl, Na₂CO₃ and NaOH - 5 g of material was contacted with 0.1 l of solution for 24 h at room temperature and the suspension was agitated in glass flasks using an orbital shaker (Marconi TM). Then, the suspension was filtrated and washed 3 times with 100 ml deionised water. The wet modified material was dried at 100°C for 24 h and subsequently used in adsorption studies.

The cation-exchange capacity of natural zeolite was determined by chemical modification (activation) with NaCl. Cation-exchange tests were made by contact of 0.25 g zeolite with 0.1 l of NH₄Cl for 2 h, using the same procedure of Mn ions adsorption.

The Mn uptake (q), expressed as Mn removal per unit mass of NCl-zeolite (mg Mn²⁺ l⁻¹), was calculated according to equation (1), where C_o is the initial Mn concentration (mg Mn²⁺ /l⁻¹), C_f is the final Mn concentration (mg Mn²⁺ l⁻¹), V is the batch volume (l) and m is the NCl-zeolite mass (g).

$$q = \frac{(C_o - C_f)V}{m} \quad (1)$$

The experiments were made in glass flasks (0.1 l) using an orbital shaker (Marconi TM) at room temperature (25°C) with constant agitation of 50 rpm.

The adsorption studies of Mn ions on zeolite were made in glass flasks, containing fixed amount of zeolite (0.25 g) and 0.1 l of solution with different Mn ions concentrations (5, 10, 25, 50, 100, 150, 300 and 600 mg l⁻¹) with initial pH of 6. The system was agitated (50 rpm) at room temperature (25°C) for a 120 min period. Supernatant aliquots were collected and subsequently filtered with 8 µm filter. The filtered materials were then analyzed.

The determination of the adsorption capacity for various equilibrium concentrations (C_f-time of contact long enough) is performed by obtaining the experimental adsorption isotherm, been commonly described by Langmuir and Freundlich models. These models are given, respectively, by the equations (2) and (3). Langmuir parameters q_{max} (mg Mn²⁺ l⁻¹) and K (mg Mn²⁺ l⁻¹) of equation (2) are the maximum capacity adsorption at high equilibrium concentrations (training adsorbent monolayer) and the equilibrium constant, respectively (Perry & Green 1999). The parameters KF (mg Mn²⁺ g⁻¹ (mg Mn²⁺ l⁻¹)^{1/n}) and 1/n (-) of equation (3) are the Freundlich capacity factor and the Freundlich intensity parameter, respectively (Weber 1972).

$$q = \frac{q_{\max} \cdot K \cdot C_f}{1 + K \cdot C_f} \quad (2)$$

$$q = K_F \cdot C_f^{1/n} \quad (3)$$

Langmuir and Freundlich data fitting were done by linearization of equations (2) and (3), given by equations (4) and (5), respectively.

$$\frac{C_f}{q} = \frac{1}{K \cdot q_{\max}} + \frac{1}{q_{\max}} \cdot C_f \quad (4)$$

$$\log q = \log K_F + \frac{1}{n} \log C_f \quad (5)$$

Results and discussion

Characterization of the Eastrhodopean zeolites

Main characteristics (chemical, mineralogical and physical properties) are summarized in Tables 1, 2 and 3. The chemical analysis shows that the zeolitized tuffs from Belia Bair deposit are K-Na-Ca dominant and those from Beli Plast deposit are Ca-K-Na dominant). Powder XRD analysis shows that the studied samples have high content of clinoptilolite – over 75%.

The values of exchangeable alkaline and alkaline-earth cations of BB- and BP-zeolites are presented in Table 4. The results indicate good ion exchange properties of the Na, K and Ca ions. These properties are directly related to the chemical composition of clinoptilolite and indicate a possible utilization in technological fields.

Photomicrographs of the Bulgarian zeolite samples, obtained by SEM, are shown in Fig. 2.

Results from static ion-exchange experiments are shown in Table 5.

Table 1. Chemical composition of the Bg-zeolite samples

Deposit Compound	Beli Bair %	Beli Plast%
SiO ₂	70,99	68,90
Al ₂ O ₃	11,78	11,50
Fe ₂ O ₃	0,83	0,76
TiO ₂	0,14	0,10
CaO	1,55	3,26
MgO	0,55	0,90
Na ₂ O	2,00	0,61
K ₂ O	4,25	2,05
LOI	7,14	11,57
Si/Al	6,02	5,99

Table 2. Mineralogical composition of the Bg-zeolite samples

Minerals	BB-zeolite,%	BP-zeolite,%
Clinoptilolite	77	82
Mordenite	-	2
Montmorillonite	9	6
Illite (clay)	4	2
Cristobalite	3	3
Plagioclase	2	2
Quartz	2	2
Other minerals	3	1

The results obtained show that the Na-enriched form of modified zeolite has biggest static ion-exchange ability. Therefore, the Na-modification leads to increasing the sorption effect of heavy metals from wastewater.

Table 3. Physical properties of the Bg-zeolite samples

Physical properties	BB-zeolite	BP-zeolite
Pore volume, cm ³ /g.	0,12	0,10
density, g/cm ³	1,06	1,16
Moisture equilibrium, %	7-8	6-7
Water absorption, %	26,0	24,0
Hardness, Mohs scale	3,5	4,0
Alkali stability, pH	7-13	7-13
Acid stability, stable after	4 N HCl; 4 h; 90 ⁰ C	4 N HCl; 4 h; 90 ⁰ C
Thermal stability	700 ⁰ C after 4 h	750 ⁰ C after 4 h
Specific surface area, m ² /g	38,83	35,26
pH	6,8-7,0	6,9-7,0
Cation-exchnage capacity for NH ₄ ⁺ , CEC, meq / 100g.	107,0	110,61

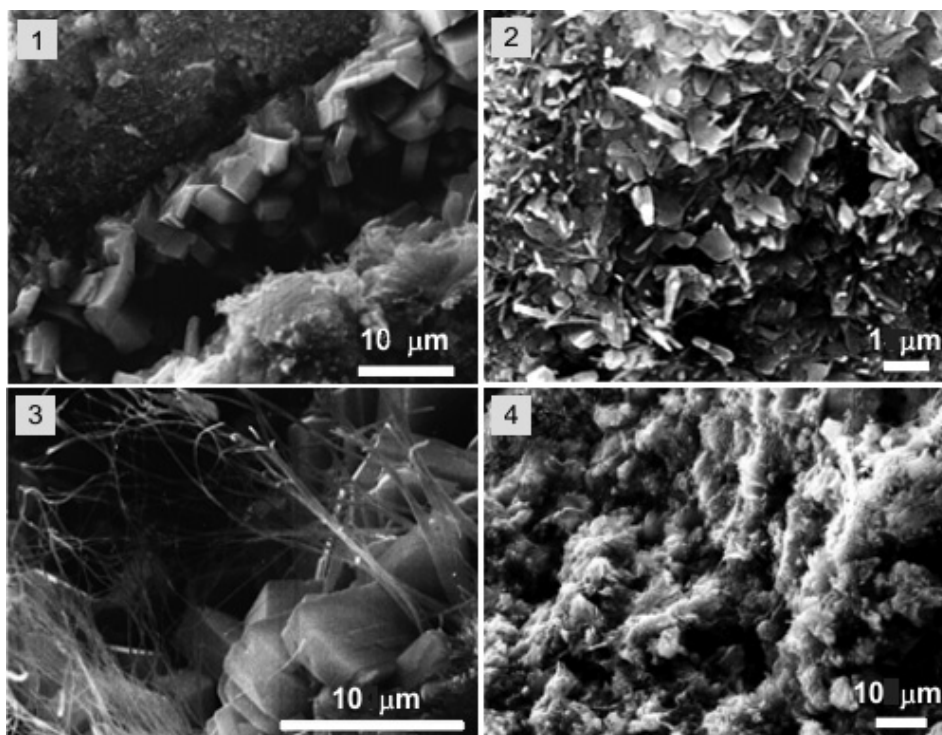


Fig. 2. SEM image presenting the morphology of the Bulgarian zeolites (Belia Bair and Beli plast deposits): (1) big platy clinoptilolite crystals; (2) small platy clinoptilolite crystals; (3) platy clinoptilolite crystals covered by mordenite needles; (4) clinoptilolite crystals between clay bands

Table 4. Ion-exchange properties of Bulgarian zeolites (meq/100g)

Exchangeable cations	BB-zeolite	BP-zeolite
Na ⁺	45,99	14,53
K ⁺	28,13	39,26
Ca ⁺	37,61	59,48
Mg ⁺	1,00	0,40
Total	112,73	113,67

Adsorption studies

Main results from these studies are presented in Fig. 3 and 4. These showed that the adsorption behavior of natural and modified zeolites with respect to heavy metal ions depends on the metal concentrations in solution.

The filter packets purify the solutions substantially lowering the metal ion

concentrations well below sanitary standard limits. The reduction of Pb²⁺ is about 18 times, Mn²⁺ – more than 20 times and Fe²⁺ and Cd²⁺ – more than 50 times. The total reduction of the heavy metals is more than 25 times and varies within the limits of 5 to 14 mg/l after the 3rd stage of treatment. Best results are obtained with blends of BB and BP natural zeolite at 50:50 ratios and after the thermo-chemical treatment.

NCl zeolites

The particle size distribution of the zeolite, obtained by means of laser diffraction method and through sieves classification is shown in Fig. 5. The figure shows that the NCl-zeolite sample has practically 100% of particles size smaller than 149 μm (100 Mesh Tyler®), and a

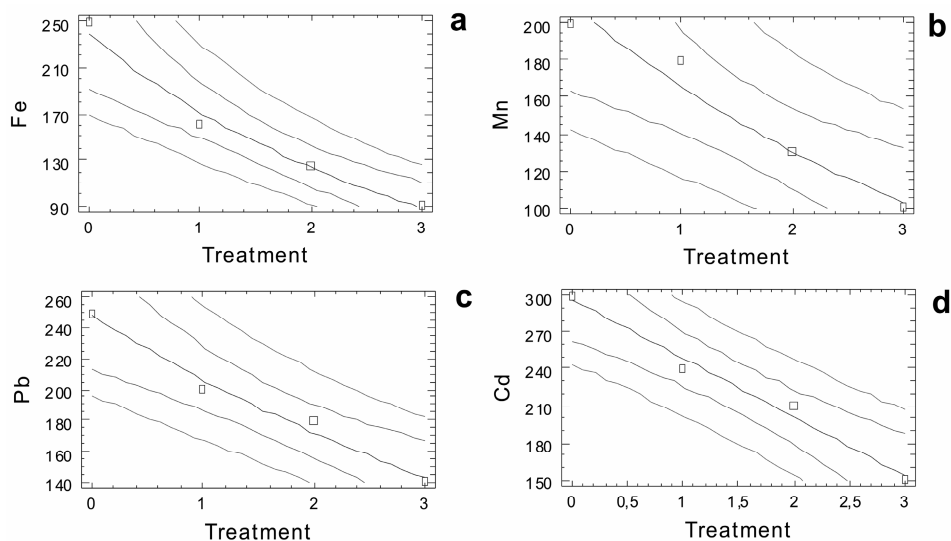


Fig. 3. (a) Exponential model: $Y = \exp(a + b \cdot X)$; $F=147,85$; $P=0.0067$; $r = -0.993$; $Fe = \exp(5,47796 - 0,331181 \cdot \text{Filters})$. (b) Exponential model: $Y = \exp(a + b \cdot X)$; $F=56.86$; $P=0.0171$; $r = -0.983$; $Mn = \exp(5,35172 - 0,240486 \cdot \text{Filters})$. (c) Exponential model: $Y = \exp(a + b \cdot X)$; $F = 92.58$; $P = 0.0106$; $r = -0,989$; $Pb = \exp(5,51532 - 0,184482 \cdot \text{Filters})$; (d) Linear model: $Y = a + b \cdot X$; $F=128.00$; $P = 0,0077$; $r = -0,992$; $Cd = 297,0 - 48,0 \cdot \text{Filters}$

large number (greater than 50%) of particles smaller than $37 \mu\text{m}$ (400 Mesh Tyler®). This size distribution favors the kinetics of the ion-exchange process because, in general, the rate of exchange is proportional to the inverse of the square of the particle diameter (Tchobanoglous et al. 2003).

The specific surface area determined by nitrogen gas adsorption (BET model) was found to be $118 \text{ m}^2 \text{ g}^{-1}$. The cation-exchange capacity for the NCl-zeolite, obtained through activation of the natural sample with NaCl, was $19.57 \text{ mg NH}_3\text{-N g}^{-1}$ ($1.1 \text{ meq NH}_4^+ \text{ g}^{-1}$). This.

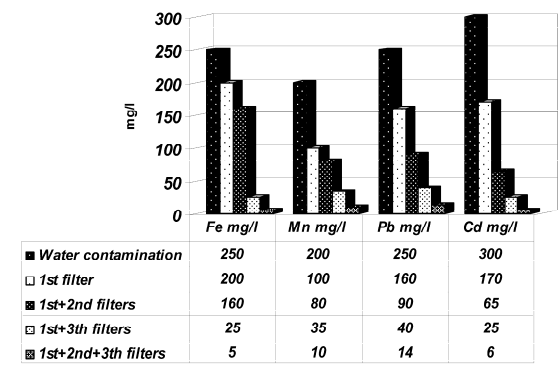


Fig. 4. Heavy metal ions composition in water after filtration

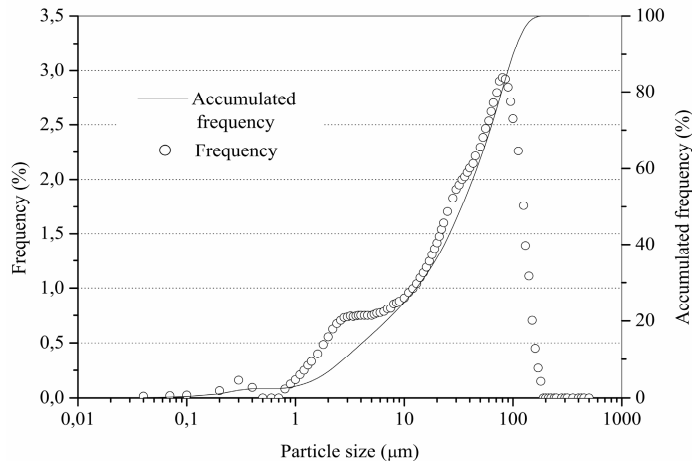


Fig. 5. Particle size distribution of the Northern Chile-zeolite

value is close to that reported by Oliveira & Rubio (2007) of $1.08 \text{ meq NH}_4^+ \text{ g}^{-1}$ and by Englert & Rubio (2005) of $1.02 \text{ meq NH}_4^+ \text{ g}^{-1}$. The results obtained for the natural sample without treatment was $8 \text{ mg NH}_3\text{-N g}^{-1}$ ($0.44 \text{ meq NH}_4^+ \text{ g}^{-1}$). The experimental error was $\pm 1.0 \text{ mg NH}_3\text{-N g}^{-1}$ ($\pm 0.055 \text{ meq NH}_4^+ \text{ g}^{-1}$).

The activation process of the NCl-zeolite clearly increases the ammonium uptake capacity by about 59%. The equivalent-based capacity were calculated according to the equivalent number of ammonium cations exchanged ($18 \text{ mg NH}_3\text{-N meq}^{-1} \text{ NH}_4^+$), since this is the main ion participating in the reaction

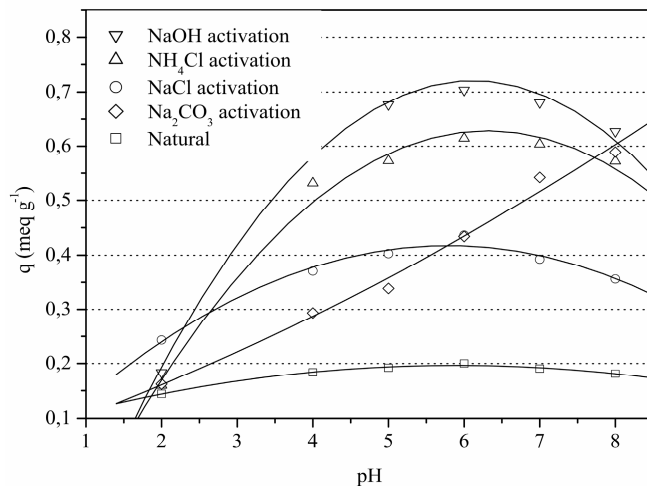


Fig. 6. Influence of pH on Mn adsorption on natural and activated NCl-zeolite. Co: $3.86 \text{ meq Mn}^{2+} \text{ l}^{-1}$; t: 120 min; [zeolite]: 2.5 g l^{-1} ; T: 25°C . Experimental error: $\pm 0.035 \text{ meq Mn}^{2+} \text{ g}^{-1}$

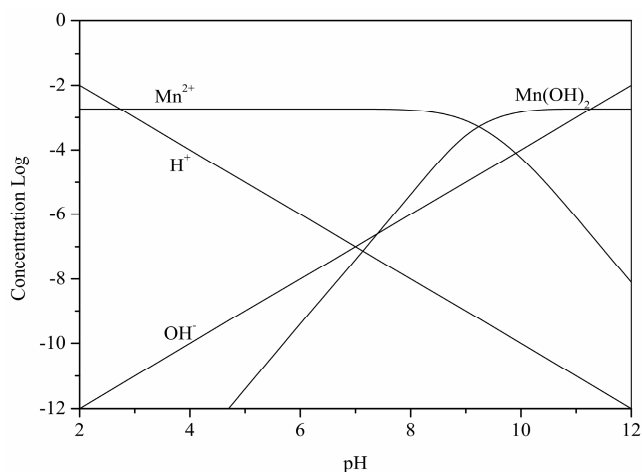


Fig. 7. Chemical diagram species for Mn aqueous solution. Co: 1 meq $\text{Mn}^{2+} \text{ l}^{-1}$.

of ionic change (Demir et al. 2002).

The pH of the aqueous solution is an important controlling parameter in the adsorption processes (Elliott & Huang 1981) and metal removal usually increases with increasing pH values (Huang & Ostovic 1978). The pH may affect the ionization degree (species formation) of the adsorbate and the surface property of the adsorbent (Lin & Yang 2002) what does not happen in the present system. The heavy metal ions may form complex with inorganic ligands such as OH^- . The extent of the compounds formation varies with the pH, the ionic composition and the particular metal concerned. Results obtained showing the influence of pH on Mn adsorption on natural and activated NCl-zeolite may be seen in Fig. 6. It shows that the adsorption of Mn ions onto zeolites increases with pH and depends on the activation type. This appears to be due to the fact that zeolites were highly selective for H_3O^+ ions when their concentration was high. Thus, at lower pH values the H_3O^+ ions competed with metal ions for the exchange sites in zeolite (Shriver et al. 1990), as can be seen in the chemical diagram constructed for a $100 \text{ mg Mn}^{2+} \text{ l}^{-1}$ aqueous solution system (Fig. 7). Figure 6 shows, that at high pH values the $\text{Mn}(\text{OH})_2$ is formed and might lead to Mn removal by precipitation and

settling. Furthermore, the active sites of the zeolite surface are slightly acidic and are deprotonated gradually with the increase of pH values resulting in increase of Mn adsorption capacity.

Conclusions

Zeolites, from different countries, showed high ion exchange and sorption properties, especially when samples become Na-enriched. Chemical and thermo-chemical modification methods of natural clinoptilolites are developed. The modification of natural zeolite in drum activator leads to oval-shape of particles and maximum contact surface. The sample NCl (Northern Chile) showed high specific surface area and cation exchange capacity of $1.1 \text{ meq NH}_4^+ \text{ g}^{-1}$. The effect of medium pH influences significantly the adsorption rate and the Mn^{2+} ions adsorption capacity and the best results were obtained at $\text{pH}=6$. The Mn^{2+} ions adsorbed amount increases with the increase of contact time, reaching the equilibrium in 60 min approximately. The Langmuir isotherm model, showed the best correlation to the equilibrium data, reaching saturation values at $0.77 \text{ meq Mn}^{2+} \text{ g}^{-1}$ ($6.5 \times 10^{-3} \text{ meq Mn}^{2+} \text{ m}^{-2}$ zeolite) for the activated zeolite with NaCl. The results also show that the cation exchange

capacity of the activated zeolites increased in relation to natural zeolite and that the activation type plays an important role in the adsorption process.

The results obtained indicate significant potential of the Bulgarian zeolites as adsorbents for wastewater using the filter packet technology at three stage treatment. This technology can be successfully used for purification of wastewaters substantially lowering the metal ion concentrations well below sanitary standard limits.

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