

# Sorption Capacities of Natural and Synthetic Zeolites for Cu(II) Ions

Joanna Kyzioł-Komosińska<sup>1\*</sup>, Czesława Rosik-Dulewska<sup>1</sup>, Małgorzata Franus<sup>2</sup>,  
Patrycja Antoszczyszyn-Szpicka<sup>3</sup>, Justyna Czupioł<sup>1</sup>, Iwona Krzyżewska<sup>1</sup>

<sup>1</sup>Institute of Environmental Engineering PAS, Curie-Skłodowska M. 30, 41-819 Zabrze, Poland

<sup>2</sup>Faculty of Civil Engineering and Architecture, University of Technology Lublin,  
Nadbystrzycka 40, 20-618 Lublin, Poland

<sup>3</sup>Regional Silesian DSc. Studies in Environmental Engineering, Central Mining Institute,  
Plac Gwarków 1, 40-166 Katowice, Poland

Received: 9 July 2014

Accepted: 23 September 2014

## Abstract

The sorption of Cu(II) ions onto natural (clinoptilolite) and synthetic (Na-X and Na-P1) zeolites was investigated. The synthetic zeolite samples were obtained from coal fly ash under hydrothermal crystallization conditions. The following issues were studied under batch conditions: the influence of the initial concentration of the Cu(II) ions, dose of zeolites, anion kind, and pH of solution. The experimental data were modelled with the Freundlich, Langmuir, and Dubinin-Radushkevich adsorption isotherms and their goodness-of-fit levels were compared. The affinity of the Cu(II) ions for synthetic zeolites was much higher than for the natural ones. The maximum sorption capacity of the synthetic zeolites (Na-P1 and Na-X) was 256 mg·g<sup>-1</sup> and 141 mg·g<sup>-1</sup>, respectively. It was 10.6 and 6 times higher, respectively, than the clinoptilolite sorption capacity (24 mg·g<sup>-1</sup>). The uptake of the Cu(II) ions occurred in two processes, i.e. the ion exchange and adsorption/precipitation in accordance with the initial concentration of the Cu(II) ions in the solution. Study of the pH and anion kind influence on the zeolite sorption capacity shows that the synthetic zeolites were effective sorbents of the Cu(II) ions, also in the acidic solutions.

The Freundlich and Dubinin-Radushkevich equations provided the best description of the sorption for the Cu(II) ions onto the synthetic zeolite systems when the initial Cu(II) ion concentration was 500-1,000 mg·L<sup>-1</sup>. On the other hand, the Langmuir and Dubinin-Radushkevich isotherms described the sorption most properly when the concentrations were above 1,000 mg·L<sup>-1</sup>.

**Keywords:** clinoptilolite, synthetic zeolites, Cu(II) ion sorption, BCR method, wastewater

## Introduction

The Water Framework Directive 2000/60/EC [1] has been in force in the EU since 2000. Its main aim is to ensure the protection of waters and help them to obtain the so-called “good” status until 2015. Accomplishing these tasks

requires identifying the threat and evaluating its influence on the environment. When necessary, it also means undertaking some remedy procedures to achieve the environmental aims in the assumed range and time concerning the “good” chemical status of waters.

Discharging industrial and municipal wastewater (rich in metal and metalloid ions) into rivers and streams is one of the many factors affecting environmental water quality.

\*e-mail: joanna.kyziol-komosińska@ipis.zabrze.pl

Although various control technologies have been applied in many industrial sources, the total quantity of the agents released to the environment remains overwhelming.

The copper ions (Cu(II)) are a hazardous pollutant of water and wastewater. The main copper sources are drainage, metallurgical and plating activities, Cu-based pesticides, agricultural practices, domestic waste, and antifouling paints. They have contributed to the progressive increase in the Cu concentration in the environment. The Cu toxicity is lower than the toxicity of other heavy metals (Cd) and metalloids (As). Unfortunately, at higher concentrations it becomes toxic and can lead to vomiting, diarrhoea, stomach cramps, and nausea. Therefore, it must be removed from wastewater. Moreover, the water quality standards for drinking water, surface water, and sewage introduced into water or to the soil, set by the Polish Ministry of Health and Ministry of the Environment [2-4], are restrictive and state that the concentrations of the Cu(II) ions should be lower than  $2.0 \text{ mg}\cdot\text{L}^{-1}$ ,  $0.05 \text{ mg}\cdot\text{L}^{-1}$ , and  $0.5 \text{ mg}\cdot\text{L}^{-1}$ , respectively.

The adsorption of heavy metal ions by various minerals (clay minerals, bentonites, zeolites, iron hydroxide) [5-10] and organogenic matter (peat, lignite) [11-13] is one of the efficient methods helping to remove these agents from wastewater.

Due to their physicochemical properties (high surface area, porosity, and cation exchange capacity), sorption affinity for inorganic and organic ions, low cost and ease of regeneration and recycling, zeolites are the most promising material for the removal of heavy metal ions from water and wastewater with sorption methods.

Zeolites make a well-defined group of minerals. They are generally regarded as hydrated silicates of aluminium, alkaline metals, and alkaline earth. They demonstrate a characteristic molecular ratio  $\text{Al}_2\text{O}_3:(\text{Na}_2, \text{K}_2, \text{Ca}, \text{Sr}, \text{Ba})\text{O}$ , which is always equal to unity and the ratio is  $\text{O}:(\text{Al}+\text{Si})=2$ .

The tetrahedron is the primary building block of the zeolite framework. Its center is occupied by a silicon or aluminum atom, with four atoms of oxygen at the vertices. The substitution of  $\text{Si}^{4+}$  by  $\text{Al}^{3+}$  defines the negative charge of the framework, which is compensated by the monovalent or divalent cations located together with water. The aluminosilicate framework is the most conserved and stable component and defines the structure type. Water molecules can be present in the voids of large cavities and bound between the framework and exchangeable ions via aqueous bridges. Water can also serve as a bridge between the exchangeable cations.

Natural zeolites exist mainly as hydrothermal forms. The most common one is clinoptilolite. Its chemical formula is  $(\text{K}_2\text{Na}_2\text{Ca})_2[(\text{Al}_6\text{Si}_{30})\text{O}_{72}]\cdot 24\text{H}_2\text{O}$  [14, 15]. Zeolites can also be obtained with the synthesis methods, such as using fly ash from coal combustion. The synthesis of zeolites from fly ash and their application in water and wastewater treatment is particularly important for the rational use of natural resources. It can also be a very cost-effective method to use fly ash.

The removal of metal ions with natural and synthetic zeolites from wastewater has been reported [16-20]. The obtained results show that zeolites can be used to remove Cu ions from wastewater and the sorption capacities of synthetic zeolites were about 10 times greater than for natural ones. However, in spite of the promising results, using these sorbents under real conditions is still quite unknown [20]. Moreover, there is no research into the binding mechanism of the sorbed Cu(II) ions and their ability to release, which is essential when the utilization mode of the used material is defined.

Our paper presents the sorption of Cu(II) ions from aqueous solutions with natural (clinoptilolite) and synthetic zeolites (Na-X and Na-P1) obtained from fly ash.

The aims of the study were to:

- (i) Investigate the capacity of the synthetic fly-ash zeolites for removing the Cu(II) ions from wastewater
- (ii) Compare the sorption capacities of the synthetic and natural zeolites for Cu(II) and the removal effectiveness of the Cu(II) ions in the presence of both zeolite groups
- (iii) Study the effect of the initial Cu(II) concentration, pH in initial solution, anion type, and zeolite dose
- (iv) Determine the ability to release the bonding ions
- (v) Estimate parameters in the sorption isotherm and determine the sorption mechanisms

## Materials and Methods

### Materials

The following minerals were used in the laboratory experiment:

- Natural zeolite – clinoptilolite from Ukraine, acquired from the Sokyrmysya deposit (Transcarpathian Region, Ukraine)
- Monomineral zeolite structures (Na-X and Na-P1), synthesized through the hydrothermal alkaline conversion of the class F fly ash from the Koziencice power station. The synthetic zeolites were obtained under the following reaction conditions:
  - Na-X: 20 g of fly ash, 0.5 L of NaOH at the concentration of  $3 \text{ mol}\cdot\text{L}^{-1}$ ,  $75^\circ\text{C}$ , 24 h [21]
  - Na-P1: 20 kg of fly ash, 12 kg of NaOH, 90 L of  $\text{H}_2\text{O}$ ,  $80^\circ\text{C}$ , 24 h [22]

The natural zeolite was used in its natural form (predominant exchange cations: Na, Ca, and K) and the synthetic zeolites as generated ones (Na-form).

### Methods

Natural and synthetic zeolites were characterized with the following parameters: morphology, mineral, and chemical composition, specific surface area, porosity, cation exchange capacity, and pH.

The morphological forms of the main zeolite components were determined with the FEI Quanta 250 FEG scanning electron microscope (SEM).

The mineral composition was determined with the powder X-ray diffraction (XRD) method. The following apparatus was used: Philips X'Pert APD diffractometer (with a PW 3020 goniometer), Cu lamp, and graphite monochromator. The analysis was performed within the angle range of 5-65 2theta. Philips X'Pert Highscore software was used to process the diffraction data. The identification of the mineral phases was based on the PDF-2 release 2010 database, formalized by the ICDD.

The chemical compositions of the zeolite samples were determined with an XRF PRIMUS II RIGAKU spectrometer. The 20% addition of the potato starch under the 20-ton pressure was applied.

The specific surface area ( $S_{\text{BET}}$ ) of the zeolite materials was determined with the  $N_2$  low-temperature adsorption/desorption method, based on the Braunauer-Emmett-Teller (BET) theory of multilayer adsorption (at  $p/p_0 = 0.06-0.3$ ). Measurements were made with the ASAP 2020 Micromeritics. Total pore volumes were estimated from single-point adsorption at a relative pressure of 0.98.

The mercury intrusion tests were performed for pressures (0.1-200 MPa) with the Carlo Erba 2000 pore-size mercury intrusion porosimeter, which is equivalent to the pore radius ranging between approx. 10.0 and  $3.8 \cdot 10^{-3}$   $\mu\text{m}$ . The cation exchange capacity (CEC) was determined with the ammonium acetate method [23].

The pH value for the zeolite suspension in water (1:10) was measured using a pH-meter with a glass electrode.

### The Sorption Experiment

The sorption capacities of the natural and synthetic zeolites for the Cu(II) ions were determined with the batch method under static conditions, contacting the solid phase (m): the Cu(II) ion solution (v) from chloride ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ) and sulphate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) solution at pH 5.0 and 3.0. The pH was  $\leq 5$  due to the  $\text{Cu}(\text{OH})_2$  precipitation at a higher pH level.

The initial Cu(II) ion solution was prepared with stock solutions containing 1,000 and 5,000  $\text{mg} \cdot \text{L}^{-1}$  of the Cu(II) ions. The working concentrations in the ranges of 0.1  $\text{mg} \cdot \text{L}^{-1}$  - 1,000  $\text{mg} \cdot \text{L}^{-1}$  and 2,000  $\text{mg} \cdot \text{L}^{-1}$  - 5,000  $\text{mg} \cdot \text{L}^{-1}$  were prepared through the serial dilution.

The zeolite doses were 10  $\text{g} \cdot \text{L}^{-1}$  and 5  $\text{g} \cdot \text{L}^{-1}$  (m:v = 1:100 and 1:200, respectively). The shaking time was 24 h. Afterward the solution was separated from the solid phase during a 20-minute centrifugation process (4,000 rpm). All the sorption samples were studied three times and the mean values are given.

The Cu(II) ion concentrations in the initial ( $C_0$ ) and equilibrium ( $C_{\text{eq}}$ ) solutions were determined with the atomic absorption spectrometer (GBC spectrometer, Avanta model). The pH values were measured in all the equilibrium solutions with a pH-meter equipped with a glass electrode.

The Cu(II) content (q) adsorbed onto the zeolites and the percentage removal of the Cu(II) ions from the solution (R) were calculated with the following formulas:

$$q = (C_0 - C_{\text{eq}}) \frac{V}{m} \quad (\text{mg} \cdot \text{g}^{-1}) \quad (1)$$

$$R = \frac{C_0 - C_{\text{eq}}}{C_0} \cdot 100\% \quad (2)$$

...where: q is the amount of the Cu(II) ions adsorbed onto zeolites ( $\text{mg} \cdot \text{g}^{-1}$ ), R is the percentage removal of the Cu(II) ions from the solution (%),  $C_0$  and  $C_{\text{eq}}$  are the initial and equilibrium concentrations of the Cu(II) ions in the solution ( $\text{mg} \cdot \text{L}^{-1}$ ), m is the sorbent mass (g) and V is the solution volume (L).

The obtained results allowed the determination of the sorption isotherms in the system of  $q=f(C_{\text{eq}})$ , and Cu(II) removal curves in the system of  $R=f(C_0)$ .

### Sorption Isotherms

The equilibrium uptake data were processed for fitting to three non-linear two-parameter isotherms:

- Freundlich – commonly used to describe the adsorption characteristics for the heterogeneous surface [24]
- Langmuir – valid for the monolayer adsorption onto a surface containing a finite number of identical sites; the model assumes uniform energies of the adsorption onto the surface and no transmigration of the adsorbate in the surface plane [25]
- Dubinin-Radushkevich – generally applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface [26]; the model is usually used to distinguish between the physical ( $E < 8 \text{ kJ} \cdot \text{mol}^{-1}$ ) and chemical adsorptions ( $8 < E < 16 \text{ kJ} \cdot \text{mol}^{-1}$ ).

The adsorption parameters were determined by transforming the equations into the linear form (linear regression method).

The isotherms and their linearized forms were given in Table 1.

### The Release Susceptibility of the Zeolite-Adsorbed Cu(II) Ions

To determine the strength of the Cu(II) ions-zeolite bonds, the BCR sequential chemical extraction method was used. It is a four-stage procedure established by the European Community Bureau of Reference. It enables the identification of the metal fractions which are bound on the positions of the exchangeable minerals (fraction I), bound to the amorphous Fe and Mn oxides (fraction II), bound to organic matter and sulphides (fraction III), and bound in the mineral structures (fraction IV) [27-29].

For sorbents, which are practically monomineral, the method helps to determine the susceptibility to the release of the adsorbed metals. It is done through establishing metal fractions in the mobile form (i.e. in the exchangeable sites of the sorption complex that are physically adsorbed; fraction I), in the mobilized form (fractions II and III) and in the forms permanently bound to the zeolite structures (fraction IV).

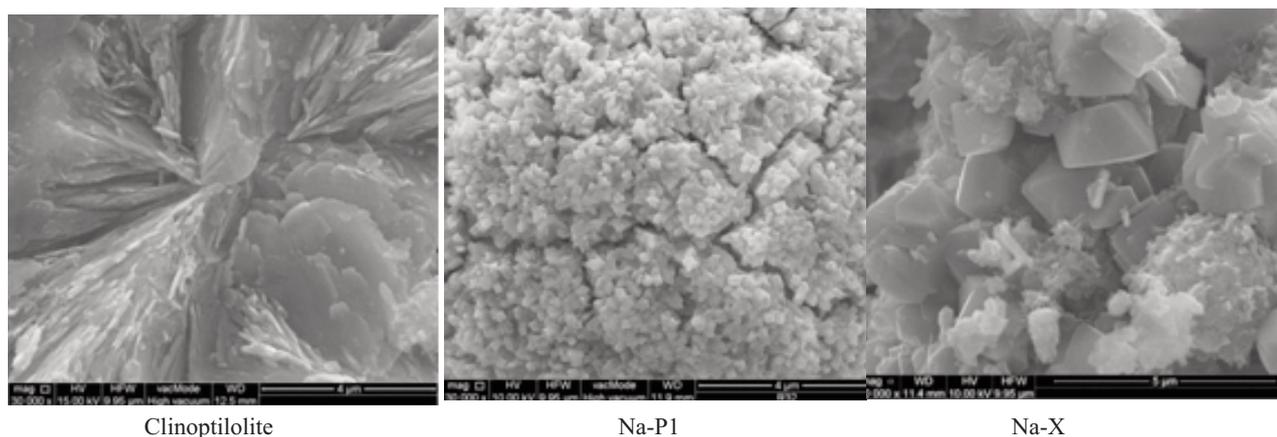


Fig. 1. Morphology and size of studied zeolites.

The bonding of the Cu(II) ions by zeolites was investigated for the zeolite samples with the Cu(II) ions adsorbed from the sulphate solutions (pH=5.0 and 3.0; initial Cu(II) concentration in the solution – 100 mg·L<sup>-1</sup> and 2,000 mg·L<sup>-1</sup>).

## Results and Discussion

### Characteristics of the Investigated Zeolites

The scanning electron microscopy (SEM) method allows obtaining more data on the size and morphology of crystallites and their clusters. The SEM images of the studied zeolites are presented in Fig. 1. Clinoptilolite occurs as 4 µm aggregates with a lamellar and acicular form.

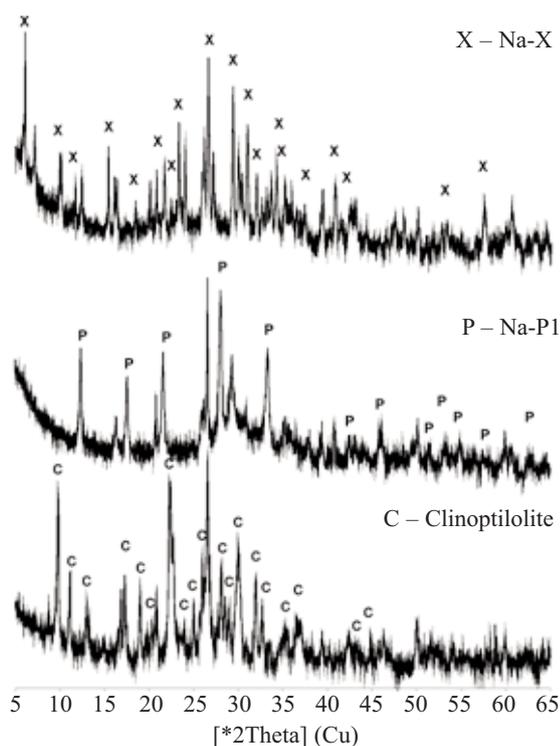


Fig. 2. The X-ray patterns of investigated zeolites.

The Na-P1 zeolite forms scaly clusters, whereas the Na-X zeolite forms isomeric crystals (2-3 µm).

The mineral compositions of the zeolite materials are shown in Fig. 2. Except for the zeolite phases, the unreacted mineral phases of fly ashes (such as mullite, quartz, and aluminosilicate glass) were found in the products of the synthesis reaction. Moreover slight amounts of Opal-CT, quartz, potassic feldspars, and mica were discovered in the mineral composition of the clinoptilolite material.

The chemical composition depended on the zeolite structure (Table 2). The analysis gives the molar Si/Al ratios of 1.17 for Na-X and 1.34 for Na-P1. The values were lower than the ratio calculated for clinoptilolite (4.79).

The physicochemical properties of the zeolite samples are given in Table 3. The results of the surface areas of the samples measured with the BET method show that higher values were obtained for both Na-P1 (86.85 m<sup>2</sup>·g<sup>-1</sup>) and Na-X (236.44 m<sup>2</sup>·g<sup>-1</sup>) in comparison to clinoptilolite (18.33 m<sup>2</sup>·g<sup>-1</sup>). Clinoptilolite also had the smallest outer surface of the pores. The total volume of the intrusion mercury was 0.586 cm<sup>3</sup>·g<sup>-1</sup>. The total surface of the clinoptilolite pores calculated with this parameter was 11.151 m<sup>2</sup>·g<sup>-1</sup>. The Na-P1 material had the largest pore surface (80.236 m<sup>2</sup>·g<sup>-1</sup>). The value for Na-X was lower (52.649 m<sup>2</sup>·g<sup>-1</sup>). The Na-X zeolite had a large number of approx. 4.34-µm pores. For clinoptilolite, there was a large number of the approx. 7.7 µm pores.

The cation exchange capacity (CEC) of zeolites depended on the Si/Al ratio framework. It decreased with the increasing Si/Al ratio (Table 3).

The natural and synthetic zeolites differed in acidity expressed with the equilibrium pH values. These values show that the precipitation of the copper hydroxide is more likely on the synthetic zeolites than on the natural ones [19].

### The Effect of the Experimental Conditions on the Sorption Processes

#### *The Initial Concentration Effect*

The sorption of the Cu(II) ions from the chloride solution (pH=5.0) onto clinoptilolite, Na-P1, and Na-X was seen

Table 1. Isotherms and their linear forms.

Isotherm model	Equation	Linear form	Plot	Eq.
Freundlich	$q=K_F C_{eq}^{1/n}$	$\log(q) = \log(K_F) + \frac{1}{n} \log(C_{eq})$	$\log(q)$ vs $\log(C_{eq})$	3.
Langmuir	$q = \frac{q_L K_L C_{eq}}{1 + K_L C_{eq}}$	$\frac{C_{eq}}{q} = \frac{1}{q_L} C_{eq} + \frac{1}{K_L q_L}$	$\frac{C_{eq}}{q}$ vs $C_{eq}$	4.
Dubinin-Radushkevich	$q=q_D \cdot \exp(-\beta \varepsilon^2)$	$\ln(q)=\ln(q_D)-\beta \varepsilon^2$	$\ln(q)$ vs $\varepsilon^2$	5.

$K_F$  – Freundlich isotherm constant ( $L \cdot g^{-1}$ ) is an approximate indicator of adsorption capacity,  $1/n$  – a function of the strength of adsorption in the adsorption process,  $q_L$  – maximum monolayer coverage capacity ( $mg \cdot g^{-1}$ ),  $K_L$  – Langmuir isotherm constant related to the affinity of binding sites ( $L \cdot mg^{-1}$ ),  $q_D$  – the sorption capacity of zeolite for Cu(II) ( $mol \cdot g^{-1}$ ),  $\beta$  – the constant ( $mol^2 \cdot J^{-2}$ ),  $\varepsilon$  – the Polanyi potential ( $J \cdot mol^{-1}$ ) equal to  $\varepsilon = RT \ln(1 + \frac{1}{C_{eq}})$ ,  $R$  – the gas constant ( $8.314 J \cdot mol^{-1} \cdot K^{-1}$ ),  $T$  – absolute temperature (K), the  $\beta$  constant was

used to determine the free energy ( $E$ ) of the adsorption:  $E = \frac{1}{(2\beta)^{1/2}}$  ( $kJ \cdot mol^{-1}$ )

Table 2. Chemical composition of studied zeolites (%).

	Clinoptilolite	Na-P1	Na-X
SiO <sub>2</sub>	73.9	44.3	41.3
Al <sub>2</sub> O <sub>3</sub>	13.6	29.0	31.4
Fe <sub>2</sub> O <sub>3</sub>	2.79	7.81	9.79
MnO	0.108	0.125	0.145
Na <sub>2</sub> O	0.63	3.97	2.43
K <sub>2</sub> O	4.02	1.19	0.809
MgO	0.297	0.513	1.22
CaO	3.75	10.7	9.2
P <sub>2</sub> O <sub>5</sub>	0.222	0.447	0.534
TiO <sub>2</sub>	0.296	1.26	2.04
Cl	0.0186	0.0186	0.0286
SO <sub>3</sub>	0.076	0.183	0.299
Si/Al ( $mol \cdot mol^{-1}$ )	4.79	1.34	1.17

as a function of the initial Cu(II) concentration. It was studied at 23°C, the metal concentration = 0.1-5,000  $mg \cdot L^{-1}$ , and m:v ratio=1:100. The results show that the uptake of the Cu(II) ions increased with the rising solution concentration and depended on the zeolite type (Fig. 3). The affinity of the Cu(II) ions for synthetic zeolites was much higher than for clinoptilolite.

For the maximum initial Cu ions concentration (5,000  $mg \cdot L^{-1}$ ), the sorption capacity of the synthetic Na-P1 and Na-X zeolites was 256  $mg \cdot g^{-1}$  and 141  $mg \cdot g^{-1}$ , respectively. It was 10.6 and 6 times higher, respectively, than the clinoptilolite sorption capacity (24  $mg \cdot g^{-1}$ ; Fig. 3a). It was also observed that Na-P1 and Na-X bound the Cu ions above their CEC. The percentage removal of the Cu(II) ions by natural and synthetic zeolites also differed significantly, which indicates various mechanisms of the Cu(II) ion bonding. The Cu(II) removal by clinoptilolite decreased with the rising initial con-

centration (from 99.8% to 4.75%). Interestingly, when the initial concentrations were 0.1-25  $mg \cdot L^{-1}$ , the Cu(II) ions were removed at a stable level (99.9%) (Fig. 3b). In the presence of Na-X and Na-P1, the Cu(II) ions were removed at this level when the initial Cu(II) ion concentration was 1,000  $mg \cdot L^{-1}$  and 500  $mg \cdot L^{-1}$ , respectively. When the initial ion concentration rose to 5,000  $mg \cdot L^{-1}$ , the removal percentage decreased to 51.82% and 28.54%, respectively. The pH values in the equilibrium solutions after sorption ( $C_0 = 1,000$  and 500  $mg \cdot L^{-1}$ ) were much higher for Na-P1 and Na-X than for clinoptilolite. They were 10.65-7.95 and 10.47-7.13 (Fig. 3c). The very high pH values for the synthetic zeolites in the

Table 3. Mineralogical composition, textural properties, cation exchange capacity, and pH of studied zeolites.

Zeolites	Clinoptilolite	Na-P1	Na-X
Mineralogical composition	Clinoptilolite	Na-P1	Na-X
	Quartz	Mullite	Mullite
	Opal	Quartz	Quartz
	Feldspar	Allumino silicate glass	Allumino silicate glass
	Mica		
Specific surface area, ( $m^2 \cdot g^{-1}$ )	18.33	86.85	236.44
Specific total pore area, ( $m^2 \cdot g^{-1}$ )	11.15	80.236	52.649
Specific micropore area, ( $m^2 \cdot g^{-1}$ )	10.65	32.84	173.45
Specific micropore volume, ( $cm^3 \cdot g^{-1}$ )	0.05	0.014	0.077
Average pore diameter, ( $\mu m$ )	0.210	0.070	0.092
Porosity, (%)	54.76	75.33	69.88
CEC, ( $cmol \cdot kg^{-1}$ )	68.98	138.7	120.3
pH	7.84	11.22	10.48

equilibrium solutions and the virtually total removal of the Cu(II) ions from the solution indicate that the Cu(II) ions precipitated as the  $\text{Cu}(\text{OH})_2$ . For the initial Cu(II) ion concentrations ranging between 2,000 and 5,000  $\text{mg}\cdot\text{L}^{-1}$ , the pH values changed in the ranges of 6.58–4.67 and 5.23–4.37, respectively. Importantly, there was no evidence of the Cu precipitation. For clinoptilolite, the pH values in the equilibrium solutions were 7.86–4.24, which indicates the bonding of ions mainly in the ion exchange reaction. The analysis of the pH-Eh diagrams for Cu-O-H shows that the Cu(II) ions can occur in the solutions whose pH that can reach 6.5–7.0 [30]. The buffer capacity and acidity of the studied zeolites depended on CEC.

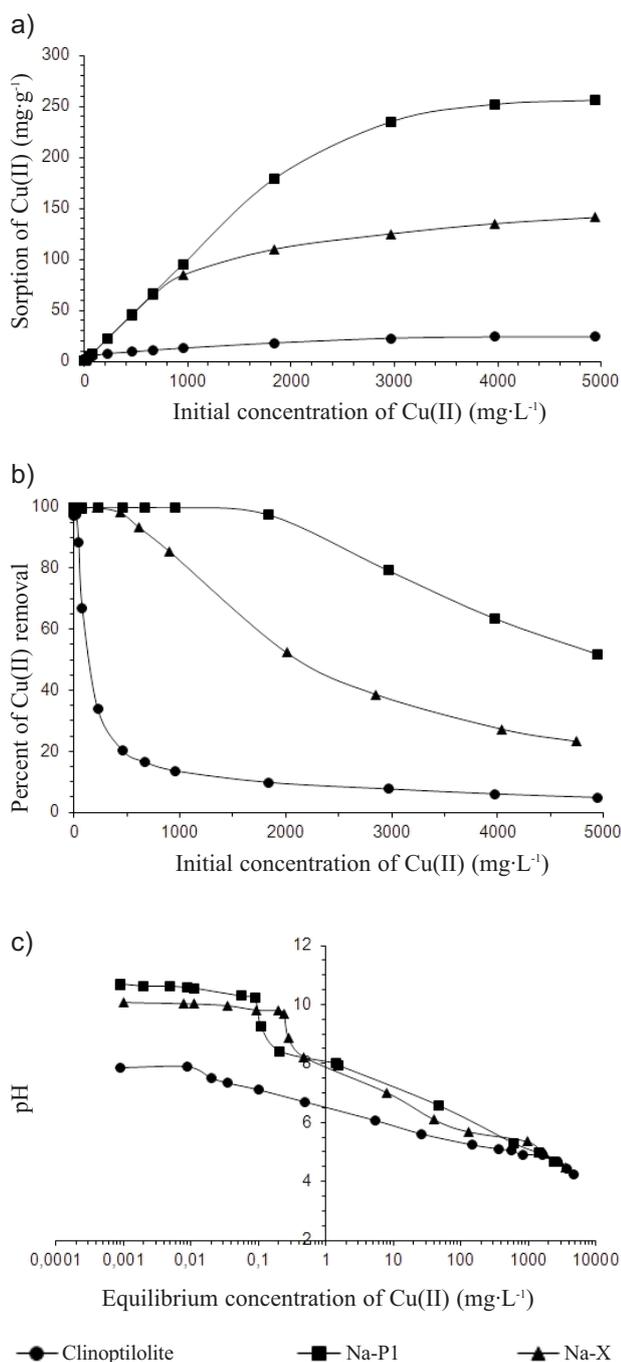


Fig. 3. Sorption capacity (a), percentage removal (b), and pH changes in equilibrium solution (c) of zeolites for Cu(II) ions.

The low correlation between the Cu(II) ion uptake and amount of exchangeable cations in the zeolites released into the solution during sorption shows that the precipitation of Cu hydroxides played a basic role in the bonding of the Cu(II) ions onto synthetic zeolites (initial Cu(II) concentration=up to 1,000  $\text{mg}\cdot\text{L}^{-1}$ ). Such a situation resulted from the high pH value in the equilibrium solutions. For the high initial Cu(II) concentration range, the ion exchange was the main bonding mechanism.

Moreover, the sorption capacities of the synthetic zeolites for the Cu(II) ions were much higher than those of clinoptilolite (up to 10 times). The finding was in accordance with the fact that the synthetic zeolites had higher CEC resulting from their lower Si:Al ratio (Table 1). The structure of zeolites (specific surface area, porosity, and average pore diameter) also had a huge impact on the number of the bound Cu(II) ions. The hydrated radius of the Cu cation is 4.19 Å. This shows that not all the channels were available for the Cu(II) ions. The crystal structure of clinoptilolite (heulandite type) exhibits three types of structural channels confined by the tetrahedral ring systems. The channels confined by 10- ( $3.0\text{Å}\times 7.6\text{Å}$ ) and eight-member rings of tetrahedra ( $3.3\text{Å}\times 4.6\text{Å}$ ) penetrating the framework from the (0 0 1) direction, intersected by channels confined by eight-membered rings of tetrahedra ( $2.6\text{Å}\times 4.7\text{Å}$ ) from the (1 0 0)-plane [31]. The crystal structure of the Na-P1 zeolite (gismondine type) presents two connected main channels penetrating the framework from the (1 0 0) direction ( $3.1\text{Å}\times 4.5\text{Å}$ ) and from the (0 1 0) direction ( $2.8\text{Å}\times 4.8\text{Å}$ ). These channels are delimited by eight-member rings of tetrahedra [31].

The microporous crystal solid of the Na-X zeolite (faujasite type) has a well-defined three-dimensional silica-alumina structure and the extra-framework exchangeable sodium cation, located in the super cage and double hexagonal rings of the framework [32, 33]. Its unit cell consists of eight supercages, eight sodalite cages and 16 hexagonal prisms. The supercages have a diameter of 13 Å, which is accessible through the 12-member ring windows (7.4 Å diameter) arranged tetrahedrally around the supercage [34].

#### Anion Type and pH Value Effects

In order to determine the influence of anion type on the uptake of the Cu(II) ions onto zeolites, the Cu(II) ion sorption from the sulphate solution was studied. The conditions were the same as for the chloride solution (i.e. pH=5.0 and 3.0; initial Cu concentration range=0.1–5,000  $\text{mg}\cdot\text{L}^{-1}$ ; m:v ratio=1:100). Afterward both sorption types were compared (Fig. 4).

The Cu(II) ion sorption on zeolites from sulphate solutions (pH=5.0) show that the anion type had little influence on the sorption capacities of the synthetic zeolites. For the Cu(II) ions, the increase in the sorption capacity of the synthetic zeolites ranged between 1% (Na-X) and 3% (Na-P1). For clinoptilolite, the anion type had a bigger influence on Cu(II) ion sorption. The maximum sorption capacity of clinoptilolite for the Cu(II) ions from the sulphate solution increased by 20.4% (28.9  $\text{mg}\cdot\text{g}^{-1}$ ). Moreover,

clinoptilolite bound a bigger number of the Cu(II) ions from more acidic solutions (pH=3.0) in the presence of sulphate ions. When the concentration was 5,000 mg·L<sup>-1</sup>, the increase in the clinoptilolite sorption capacity was 40%. For the synthetic zeolites, the anion-type influence on the sorption capacities was slighter. The maximum Na-P1 sorption capacity increased by 10% (from 193 mg·g<sup>-1</sup> to 213 mg·g<sup>-1</sup>). The Na-X sorption capacity did not change at all (Fig. 4).

The conducted research also helped to determine the influence of the initial concentration pH on the zeolite sorption capacities. The solution pH did not have any impact on the initial Cu(II) concentrations when the values were up to 50 mg·L<sup>-1</sup> (clinoptilolite) and 500 mg·L<sup>-1</sup> (synthetic zeolites). Above these levels, the sorption of the Cu(II) ions from the more acidic solutions (pH=3.0) was

lower than from the less acidic ones (pH=5.0). It depended on both the anion and zeolite types. The maximum sorption capacity of clinoptilolite decreased by 40% (from 28.9 mg·g<sup>-1</sup> to 17.4 mg·g<sup>-1</sup>) in the presence of sulphate ions and by 48% (from 24 mg·g<sup>-1</sup> to 12.4 mg·g<sup>-1</sup>) in the presence of chloride ions.

The changes in the sorption capacities of the synthetic zeolites were slighter:

- Na-P1 – the sorption capacity decreased by 19.3% (from 264 to 213 mg·g<sup>-1</sup>) in the presence of the sulphate ions and by 24.6% (from 256 to 193 mg·g<sup>-1</sup>) in the presence of the chloride ions
- Na-X – the sorption capacity was lower by 22% (from 140 to 110 mg·g<sup>-1</sup>) regardless of the anion type (Fig. 4). The obtained results show that the synthetic zeolites make effective sorbents of the Cu(II) ions, also from acidic

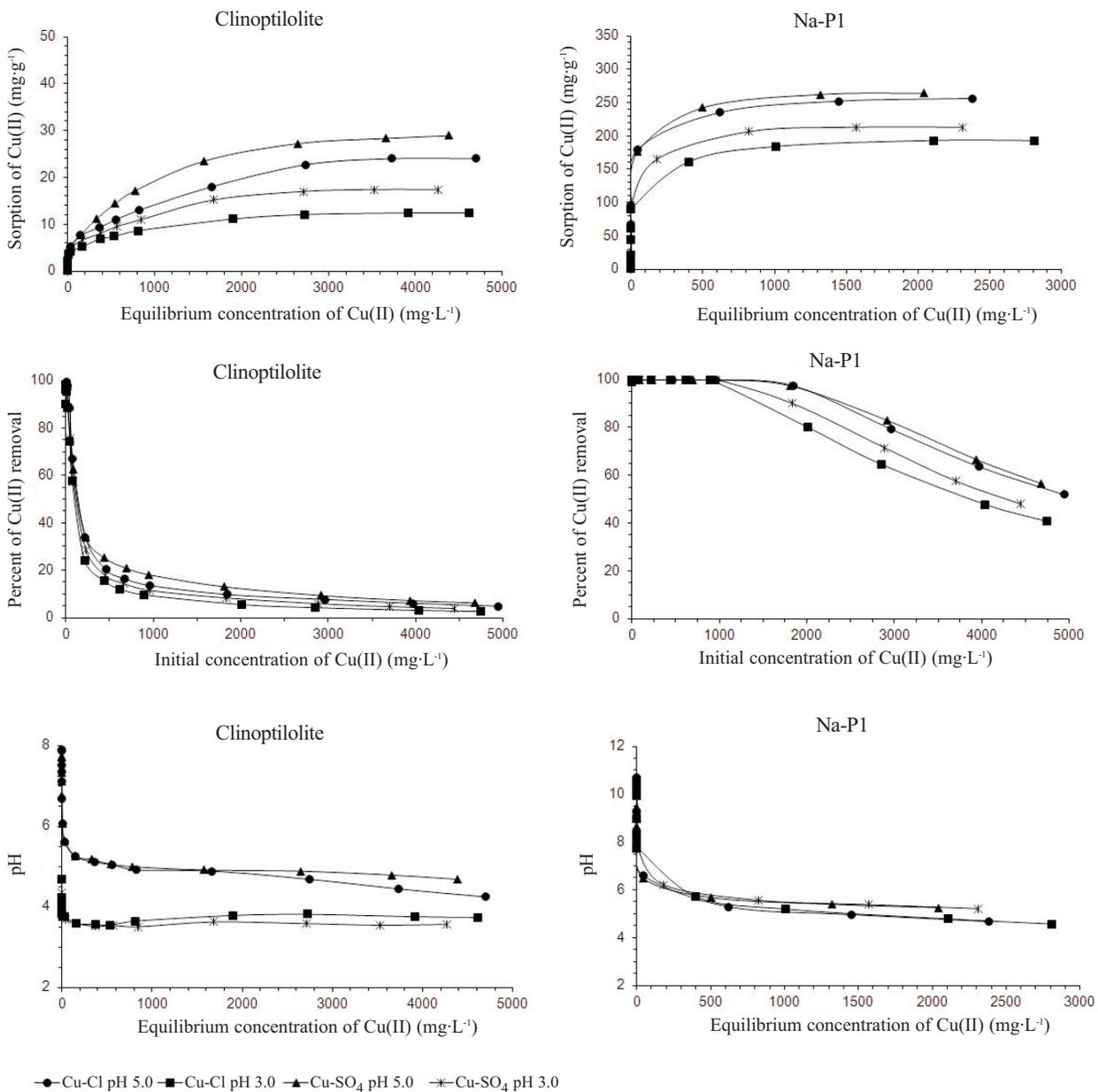


Fig. 4. Effect of anion type and initial pH on sorption capacities, percentage removal, and pH changes in equilibrium solution of clinoptilolite and Na-P1 for Cu(II) ions.

Table 4. Effect of sorbent dose onto sorption capacities of zeolites for Cu(II) and their removal from solution (at  $C_0$  100 mg·L<sup>-1</sup> and 5,000 mg·L<sup>-1</sup>).

Solution	Dose of sorbent, g·L <sup>-1</sup>	$C_0$ , mg·L <sup>-1</sup>	Clinoptilolite, mg·g <sup>-1</sup> (%)	Na-P1, mg·g <sup>-1</sup> (%)	Na-X, mg·g <sup>-1</sup> (%)
Cl <sup>-</sup> , pH 5.0	10	100	5.25 (66.9)	7.89 (99.9)	7.86 (99.5)
		5,000	24.0 (4.85)	256 (51.8)	140 (28.54)
	5	100	8.86 (57.86)	14.9 (99.90)	14.92 (99.46)
		5,000	49.7 (5.03)	276 (27.93)	144 (14.56)
Cl <sup>-</sup> , pH 3.0	10	100	4.2 (57.5)	7.89 (99.9)	7.27 (99.8)
		5,000	12.4 (2.6)	256 (51.8)	110 (23.21)
	5	100	6.48 (37.24)	14.99 (99.9)	17.36 (99.8)
		5,000	15.73 (1.61)	276 (27.93)	124 (12.91)
SO <sub>4</sub> <sup>2-</sup> , pH 5.0	10	100	5.14 (62.68)	8.19 (99.9)	8.17 (99.6)
		5,000	28.9 (6.17)	264 (56.41)	141 (29.91)
	5	100	8.9 (60.95)	14.59 (99.9)	14.57 (99.63)
		5,000	56 (5.98)	279 (29.85)	153 (16.33)
SO <sub>4</sub> <sup>2-</sup> , pH 3.0	10	100	6.0 (57.47)	8.7 (99.7)	8.6 (99.5)
		5,000	17.4 (3.91)	213 (47.97)	108 (24.32)
	5	100	7.16 (41.15)	17.39 (99.9)	17.31 (99.45)
		5,000	23.7 (2.50)	229 (24.15)	116 (12.21)

solutions. Furthermore, Balintova [35] showed that the natural zeolites were highly efficient in removing the Cu(II) ions from acidic solutions. The finding was confirmed in this study only for the low concentrations of the Cu(II) ions (initial solution = up to 5 mg·L<sup>-1</sup>).

In summary, the research results indicate that the zeolite sorption capacity for the Cu(II) ions changed in the following order:

$$q(\text{SO}_4^{2-}, \text{pH } 5.0) > q(\text{Cl}^-, \text{pH } 5.0) > q(\text{SO}_4^{2-}, \text{pH } 3.0) > q(\text{Cl}^-, \text{pH } 3.0)$$

The results demonstrate that Na-P1 had a higher affinity for metal ions than other zeolites.

The Cu(II) ion removal occurred in two processes, i.e. the ion exchange with the Na<sup>+</sup> ions and adsorption/precipitation. The Cu(II) ions moved through the zeolite pores and channels and were exchanged with the Na<sup>+</sup> ions.

#### The Zeolite Dose Effect

Table 4 presents the results for the sorption of the Cu(II) ions on clinoptilolite and the synthetic zeolites expressed in mg·g<sup>-1</sup> and %, at the 100 mg·L<sup>-1</sup> and 5,000 mg·L<sup>-1</sup> initial concentrations and for two zeolite doses (10 g·L<sup>-1</sup> and 5 g·L<sup>-1</sup>). When the zeolite dose was lowered in the same solution volume, the sorption capacity of the zeolite increased in accordance with formula 1. For clinoptilolite, when the sorbent dose was twice as low, the sorption capacity increased

by 1.2-1.73 (100 mg·L<sup>-1</sup> concentration) and by 1.36-2.0 (5,000 mg·L<sup>-1</sup> concentration). For the synthetic zeolites, when the sorbent dose was twice as low, the sorption capacity doubled (100 mg·L<sup>-1</sup> initial concentration) or increased by 7-12% (5,000 mg·L<sup>-1</sup> concentration). When the sorbent dose was lowered, the removal percentage decreased.

When transforming Eq. 1 and substituting it in Eq. 2, the dependence of %R =  $\frac{q \cdot m}{C_0 \cdot V} \cdot 100$  is obtained. This indicates that the removal percentage is proportional to the sorbent mass.

The obtained results confirmed the correlation (Table 4). Both the sorption capacity and the effectiveness of the pollutant removal should be taken into consideration when the sorption process is optimized and the sorbent dose is determined.

#### Sorption Isotherms

The sorption data were fitted to the Freundlich, Langmuir, and Dubinin-Radushkevich equations and were shown in Fig. 5. The estimated values of the parameters in the isotherm equations and the determination coefficient (showing the adjustment of the sorption data to the isotherm equations) are given in Table 5.

All the isotherms demonstrated the same trends in the changes of the parameter values. The determination coefficient value ( $R^2 > 0.95$ ) indicates a strong positive cor-

relation for the data. It also demonstrates that the sorption data of the Cu(II) ions onto zeolites are well-described with the Langmuir and Dubinin-Radushkevich isotherms. The Freundlich isotherm ( $R^2$  was 0.7542-0.9209) describes the process less favorably.

The  $1/n$  values calculated from the Freundlich isotherm were 0-1, which states that the sorption of the Cu(II) ions onto zeolites was favourable. The  $1/n$  and  $K_F$  (Freundlich

isotherm) and  $q_L$  and  $K_L$  (Langmuir isotherm) constants increased with pH, which indicates that the sorption was more favourable and the sorption capacity and intensity were enhanced at a higher pH. The  $E$  value (Dubinin-Radushkevich equation) was above  $8 \text{ kJ}\cdot\text{mol}^{-1}$ , which points to the ion exchange process. Nonetheless, for all the Cu(II) ions-zeolite systems, the estimated  $q_L$  parameter was lower than the maximum sorption capacity determined experi-

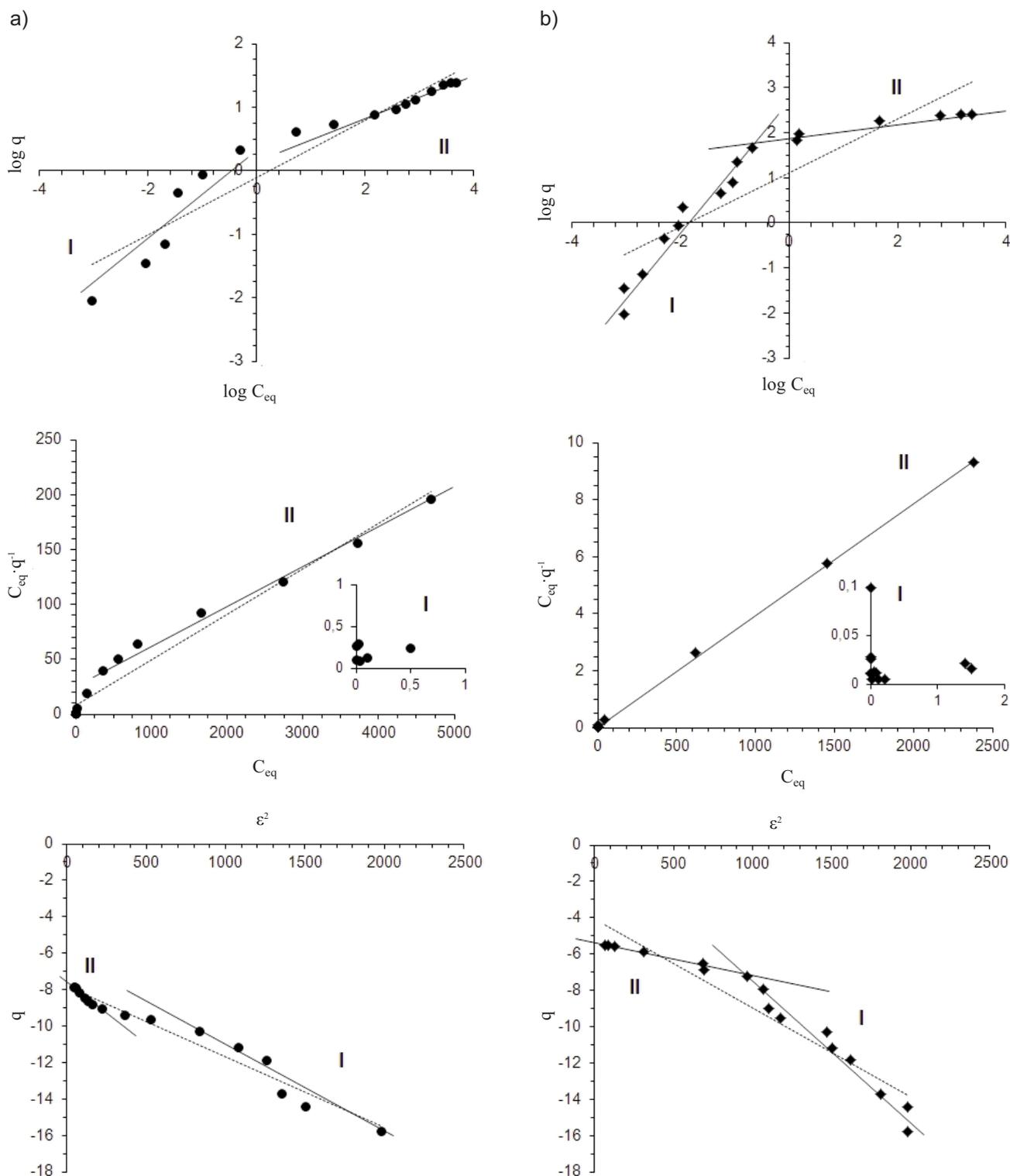


Fig. 5. Fitting lines of Freundlich, Langmuir, and Dubinin-Radushkevich isotherms of Cu(II) ions onto clinoptilolite (a) and Na-P1 (b) zeolites.

Table 5. The isotherm constants for the adsorption of Cu(II) ions onto zeolites.

		Cu-Cl pH 5.0			Cu-Cl pH 3.0			Cu-SO <sub>4</sub> pH 5.0			Cu-SO <sub>4</sub> pH 3.0		
		All C <sub>0</sub>	I C <sub>0</sub>	II C <sub>0</sub>	All C <sub>0</sub>	I C <sub>0</sub>	II C <sub>0</sub>	All C <sub>0</sub>	I C <sub>0</sub>	II C <sub>0</sub>	All C <sub>0</sub>	I C <sub>0</sub>	II C <sub>0</sub>
		F	0.4676	0.9398	0.2819	0.4455	0.8745	0.2273	0.4638	0.9405	0.3766	0.4706	0.8656
L	K <sub>F</sub> (L·g <sup>-1</sup> )	0.8129	3.0621	2.1149	0.4964	1.4832	1.8655	0.8669	5.4001	1.325	0.5474	0.1816	1.723
	R <sub>2</sub> (-)	0.8996	0.9321	0.9613	0.8855	0.8922	0.9801	0.9209	0.9382	0.9845	0.9051	0.8879	0.9819
Clinop.	q <sub>max</sub> (mg·g <sup>-1</sup> )	24.00	9.20	24.00	12.40	7.81	12.40	28.90	11.36	28.90	17.40	10.60	17.40
	q <sub>L</sub> (mg·g <sup>-1</sup> )	24.21	9.58	26.04	12.52	3.43	13.01	29.14	7.93	31.18	17.67	3.33	18.70
	K <sub>L</sub> (L·mg <sup>-1</sup> )	0.00489	0.6229	0.00217	0.00868	0.5661	0.00407	0.0054	0.8277	0.00242	0.00659	0.5917	0.00301
	R <sub>2</sub> (-)	0.9682	0.0049	0.9736	0.9917	0.0213	0.9992	0.9768	0.0992	0.9846	0.9828	0.0217	0.9870
	β (mol <sup>2</sup> ·kJ <sup>-2</sup> )	0.0039	0.0039	0.0091	0.0041	0.0043	0.0053	0.00398	0.00398	0.00723	0.0043	0.0044	0.0071
D-R	q <sub>D</sub> (mol·g <sup>-1</sup> )	0.388	0.378	0.589	0.262	0.291	0.251	0.484	0.471	0.652	0.342	0.353	0.386
	R <sub>2</sub> (-)	0.9624	0.9432	0.9775	0.9533	0.9348	0.9569	0.9661	0.9482	0.9758	0.9599	0.9908	0.9439
	E (kJ·mol <sup>-1</sup> )	11.32	11.32	8.41	11.04	10.78	9.71	11.20	11.21	8.31	10.78	10.66	8.45
Na-PI	1/n (-)	0.5991	1.1452	0.1342	0.5262	1.1377	0.1029	0.6065	1.831	0.1386	0.5740	1.065	0.1064
	K <sub>F</sub> (L·g <sup>-1</sup> )	12.81	123.1	96.09	11.329	160.7	1.942	13.46	200.9	97.49	10.83	75.88	96.58
	R <sub>2</sub> (-)	0.7910	0.9344	0.9703	0.7542	0.9299	0.9959	0.8010	0.9779	0.9859	0.8054	0.9478	0.9925
	q <sub>max</sub> (mg·g <sup>-1</sup> )	256.0	95.45	256.0	193.0	89.45	193.0	264.0	95.09	264.0	213	95.7	213.0
	q <sub>L</sub> (mg·g <sup>-1</sup> )	255.1	248.9	257.4	192.7	151.29	196.0	263.8	3.147	265.9	213.3	-44.09	215.9
L	K <sub>L</sub> (L·mg <sup>-1</sup> )	0.1122	0.1835	0.0397	0.1016	0.3557	0.02166	0.1175	1.819	0.0578	0.1146	-0.8145	0.03468
	R <sub>2</sub> (-)	0.9995	0.0074	0.9995	0.9993	0.0102	0.9993	0.9995	0.2335	0.9995	0.9995	0.0844	0.9995
D-R	β (mol <sup>2</sup> ·kJ <sup>-2</sup> )	4.90	6.79	1.60	4.4	0.0067	0.0012	0.0049	0.0066	0.00158	0.0047	0.0058	0.00118
	q <sub>D</sub> (mol·g <sup>-1</sup> )	16.25	295.5	4.54	10.92	350.7	3.24	17.4	238.4	4.69	11.27	62.6	3.59
	R <sub>2</sub> (-)	0.9126	0.9556	0.9985	0.8844	0.9484	0.9954	0.9192	0.9619	0.9980	0.9201	0.9420	0.9812
E (kJ·mol <sup>-1</sup> )	10.10	8.58	17.67	10.66	8.638	20.41	10.10	10.10	8.70	17.78	9.28	20.58	

Table 5. Continued.

	Cu-Cl pH 5.0			Cu-Cl pH 3.0			Cu-SO <sub>4</sub> pH 5.0			Cu-SO <sub>4</sub> pH 3.0		
	All C <sub>0</sub>	I C <sub>0</sub>	II C <sub>0</sub>	All C <sub>0</sub>	I C <sub>0</sub>	II C <sub>0</sub>	All C <sub>0</sub>	I C <sub>0</sub>	II C <sub>0</sub>	All C <sub>0</sub>	I C <sub>0</sub>	II C <sub>0</sub>
	1/n (-)	0.5750	0.9493	0.1595	0.5689	1.234	0.154	0.5761	1.151	0.1465	0.5668	1.134
K <sub>F</sub> (L·g <sup>-1</sup> )	4.059	14.59	38.64	3.358	27.61	32.45	4.248	2.107	43.58	4.549	20.61	40.25
R <sub>2</sub> (-)	0.8721	0.9417	0.9921	0.8459	0.9740	0.9680	0.8797	0.9488	0.9974	0.8515	0.9826	0.9400
q <sub>max</sub> (mg·g <sup>-1</sup> )	141.0	84.70	141.0	110.0	76.7	110.0	140.0	85.1	140.0	108.0	84.3	108.0
q <sub>L</sub> (mg·g <sup>-1</sup> )	137.6	81.26	142.57	110.47	4.261	110.9	138.1	-89.35	141.8	107.9	101.23	108.7
K <sub>L</sub> (L·mg <sup>-1</sup> )	0.03159	0.0503	0.0145	0.05787	1.945	0.0335	0.04079	-3.464	0.01163	0.0672	0.1367	0.02987
R <sub>2</sub> (-)	0.9964	0.0116	0.9958	0.9998	0.6678	0.9996	0.9984	0.0323	0.9985	0.9997	0.3327	0.9997
β (mol <sup>2</sup> ·kJ <sup>-2</sup> )	0.0047	0.0053	0.0026	0.00503	0.00603	0.00208	0.0047	0.0053	0.0025	0.0049	0.0059	0.00175
q <sub>D</sub> (mol·g <sup>-1</sup> )	4.34	9.88	2.45	4.21	15.08	1.98	4.49	9.94	2.52	4.29	16.8	1.89
R <sub>2</sub> (-)	0.9552	0.9427	0.9785	0.9472	0.9538	0.9634	0.9615	0.9631	0.9996	0.9571	0.9631	0.9881
E (kJ·mol <sup>-1</sup> )	10.31	9.71	13.87	9.97	9.10	15.50	10.31	9.71	14.14	10.10	9.71	16.90

mentally (q<sub>m</sub>) (Table 5). Moreover, the experimental points in the plot of log q vs log C<sub>eq</sub>, C<sub>eq</sub>/q vs C<sub>eq</sub> and q vs. ε<sup>2</sup> showed the data were grouped in the two initial concentration ranges (I and II), where the sorption of the Cu(II) ions onto zeolites had a similar mechanism (Fig. 5). The concentration ranges depended on the zeolite type:

- Clinoptilolite – 0.1-25 mg·L<sup>-1</sup> for range I, and 50-5,000 mg·L<sup>-1</sup> for range II
- Na-P1 – 0.1-1,000 mg·L<sup>-1</sup> for range I, and 2,000-5,000 mg·L<sup>-1</sup> for range II
- Na-X – 0.1-500 mg·L<sup>-1</sup> for range I, and 750-5,000 mg·L<sup>-1</sup> for range II

When analyzing the sorption conditions, it was observed that the ranges were determined by zeolite acidity, which was shown by the equilibrium pH. For clinoptilolite, it was 7.86-6.85 (range I) and 6.69-4.24 (range II). For Na-P1 and Na-X, the pH was 10.65-7.75 and 10.47-7.13 (range I), respectively. The values for range II were below 7, i.e. 6.58-4.67 (Na-P1) and 6.48-4.37 (Na-X).

For the sorption data in both initial concentration ranges, the parameters in three isotherms and determination coefficient were determined. The information is presented in Table 5.

The Cu(II) ion sorption on clinoptilolite was well-described with the Freundlich and Dubinin-Radushkevich equations in range I (low initial concentration range). This could not be described with the Langmuir equation. All the equations were useful for describing the Cu(II) ion sorption at higher concentration levels. The 1/n parameter value for both concentration ranges <1 indicates a favourable sorption. The E parameter (Dubinin-Radushkevich equation) ranged between 10.78 and 11.32 kJ·mol<sup>-1</sup>, which shows the sorption had an ion-exchange character at a low concentration range. For range II, the E parameter was 8.31-8.71 kJ·mol<sup>-1</sup>, which points to the physical sorption.

The Freundlich and Dubinin-Radushkevich equations described well the Cu(II) ion sorption onto the synthetic zeolites in range I. The isotherm models that take into account certain heterogeneity seem to have an advantage over the Langmuir isotherm [34]. The estimated 1/n value was above 1 and indicated the cooperative sorption. The Cu(II) ion sorption cannot be described with the Langmuir equation. The E parameter was 8.28-8.71 kJ·mol<sup>-1</sup> (physical sorption). For range II, the Langmuir and Dubinin-Radushkevich equations were the most appropriate to describe sorption (R<sup>2</sup>>0.99). The maximum capacity of the q<sub>L</sub> monolayer was higher than the maximum experimental sorption (q<sub>m</sub>). The E parameter value was 13.87-20.58 kJ·mol<sup>-1</sup> and pointed to the ion exchange.

### The Bonding of Cu(II) Ions by the Investigated Zeolites

The sequential extraction results confirmed different bonding mechanisms of the Cu(II) ions by clinoptilolite and synthetic zeolites. They also pointed to the presence of the exchangeable sites in the zeolites. The sites differed in their positions and coordination number of the oxygen atoms.

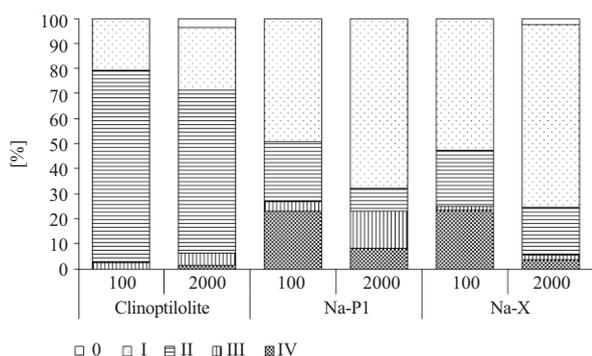


Fig. 6. Sorption pools of different binding strength for Cu(II) ions binding onto zeolites.

Clinoptilolite bound the ions mainly in the fraction II (adsorbed Cu(II) ions released in the reaction with hydroxylammonium chloride, pH=3.5), at the level of 77%. Approx. 20% of the adsorbed ions occurred in the exchangeable sites (fraction I). The researchers did not observe a significant influence of the initial Cu(II) ion concentration on their release susceptibility.

The release susceptibility of the Cu(II) ions absorbed onto the synthetic zeolites largely depended on the initial concentration of the Cu(II) ions in the solution and did not depend on the zeolite type. When the initial concentration was 100 mg·L<sup>-1</sup>, the Cu(II) ions were bound by Na-P1 and Na-X on the exchangeable positions (fraction I) at levels of 49.2%, 52.4% and 23.8%, 22.6% in fraction II, respectively. Importantly, the Cu(II) ion content was very high in fraction IV (23.17% and 22.59%). The increase in the initial concentration of the Cu(II) ions to 2,000 mg·L<sup>-1</sup> resulted in the increase of ions in the ion-exchange bonds to 67.7% and 72.8%. The ion number decreased in the immobilized bonds (fraction IV) to 8.08% and 3.5% of the adsorbed amount (Fig. 6).

## Conclusions

The research shows that synthetic zeolites have very good sorption capacities for the Cu(II) ions, both at low and high concentration levels. Consequently, they should be taken into consideration as effective and economical sorbents for water and wastewater treatment. They can also be used for acidic water and wastewater. The affinity of the Cu(II) ions for the synthetic zeolites was much higher than for the natural clinoptilolite. The maximum sorption capacity of the synthetic zeolites was 256 mg·g<sup>-1</sup> (Na-P1) and 141 mg/g (Na-X). It was 10.6 and 6 times higher, respectively, than the clinoptilolite sorption capacity (24 mg·g<sup>-1</sup>).

The zeolite sorption capacity for the Cu(II) ions depended on the initial solution pH and changed in the following order:

$$q(\text{SO}_4^{2-}, \text{pH}=5.0) > q(\text{Cl}^-, \text{pH}=5.0) > q(\text{SO}_4^{2-}, \text{pH}=3.0) > q(\text{Cl}^-, \text{pH}=3.0)$$

The removal of the Cu(II) ions occurred in the two main processes, i.e. the ion exchange with the Na<sup>+</sup> ions and adsorption/precipitation. It depended on the initial concentration of the Cu(II) ions in the solution, which was corroborated with the sequential extraction results.

The Freundlich and Dubinin-Radushkevich equations provided the best description of the sorption for the Cu(II) ions onto the synthetic zeolites, when the initial Cu(II) ion concentration was 500-1,000 mg·L<sup>-1</sup>. On the other hand, the Langmuir and Dubinin-Radushkevich isotherms described the sorption most properly when the concentrations were above 1,000 mg·L<sup>-1</sup>. The E parameter value (Dubinin-Radushkevich Eq.) indicated the physical sorption and ion exchange, respectively.

## Acknowledgements

The research was conducted within the framework of statutory research by the Institute of Environmental Engineering Sciences, Polish Academy of Sciences in Zabrze in 2013-2014.

## References

1. DIRECTIVE 2000/60/EC of THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 23 October 2000 establishing a framework for Community action in the field of water policy, **2000**.
2. Regulation of the Minister of Environment dated 9 November 2011 on classification of bodies of surface water and environmental quality standards for priority substances. Journal of Laws No. 257, Item 1545, **2011** [In Polish].
3. Regulation of the Minister of Environment dated 24 July 2006 on conditions to be met when discharging sewage to waters or to the soil and on substances of particular adverse impact on the water environment. Journal of Laws No. 137, Item 984, **2006** [In Polish].
4. Regulation of the Minister of Health dated 29 March 2007 on the requirements related to the quality of water intended for human consumption. Journal of Laws No. 61, Item 417, **2007** [In Polish].
5. GHOMRI F., LAHSINI A., LAAJEB A., ADDAOU A. The Removal of heavy metal ions (copper, zinc, nickel and cobalt) by natural bentonite. Larhyss J. **12**, 37, **2013**.
6. MELICHOVA Z., HROMADA L. Adsorption of Pb<sup>2+</sup> and Cu<sup>2+</sup> ions from aqueous solutions on natural bentonite. Pol. J. Environ. Stud. **22**, 457, **2013**.
7. KYZIOL-KOMOSINSKA J., BARBA F., CALLEJAS P., ROSIK-DULEWSKA C. Beidellite and other natural low-cost sorbents to remove chromium and cadmium from water and wastewater. Bol. Soc. Esp. Cerám. Vidr. **49**, 121, **2010**.
8. ZHU J., HUANG Q., PIGNA M., VIOLANTE A. Competitive sorption of Cu and Cr on goethite and goethite-bacteriacomplex. Chem. Eng. J. **179**, 26, **2012**.
9. ANIELAK A. M., SCHMIDT R. Sorption of lead and cadmium cations on natural and manganese-modified zeolite. Pol. J. Environ. Stud. **20**, 15, **2011**.
10. FRANUS M., BANDURA L. Sorption of heavy metal ions from aqueous solution by glauconite. Fresen. Environ. Bull. **23**, 825, **2014**.

11. KYZIOŁ J. Effect of physical properties and cation exchange capacity on sorption of heavy metals onto peats. *Pol. J. Environ. Stud.* **11**, 713, **2002**.
12. DOSKOČIL L., PEKAŘ M. Removal of metal ions from multi-component mixture using natural lignite. *Fuel Process. Technol.* **101**, 29, **2012**.
13. JANOŠ P., SYPECKÁ J., MLČKOVSKÁ P., KURÁŇ P., PILAŘOVÁ V. Removal of metal ions from aqueous solutions by sorption onto untreated low-rank coal (oxihumolite). *Sep. Purif. Technol.* **53**, 322, **2007**.
14. WANG S., PENG Y. Natural zeolites as effective adsorbents in water and wastewater treatment. *Chem. Eng. J.* **156**, 11, **2010**.
15. FRANUS W., DUDEK K. Clay minerals and clinoptilolite of variegated shales formation of the Skole Unit, Polish Flysch Carpathians. *Geol. Carpath.* **50**, 23, **1999**.
16. PANAYOTOVA M. I. Kinetics and thermodynamics of copper ions removal from wastewater by use of zeolites. *Waste Manage.* **21**, 671, **2001**.
17. KESRAOUI-OUKI S., CHEESEMAN C. R., PERRY R. Natural zeolite utilisations in pollution control: a review of applications to metals effluents. *J. Chem. Tech. Biotechnol.* **59**, 121, **1994**.
18. ČURKOVIĆ L., CERJAN-STEFANOVIĆ Š., FILIPAN T. Metal ion exchange by natural and modified zeolites. *Water Res.* **31**, 1379, **1997**.
19. PERIĆ J., TRGO M., VUKOJEVIĆ MEDVIDOVIĆ N. Removal of zinc, copper and lead by natural zeolite—a comparison of adsorption isotherms. *Water Res.* **38**, 1893, **2004**.
20. ALVAREZ-AYUSO E., GARCIA-SANCHEZ A., QUEROL X. Purification of metal electroplating waste waters using zeolites. *Water Res.* **37**, 4855, **2003**.
21. FRANUS W. Characterization of X-type zeolite prepared from coal fly ash. *Pol. J. Environ. Stud.* **21**, 337, **2012**.
22. WDOWN M., FRANUS M., PANEK R., BANDURA L., FRANUS W. The conversion technology of fly ash into zeolites. *Clean Techn. Environ. Policy* **16**, 1217, **2014**.
23. TAN K. H. Soil sampling, preparation and analysis. Marcel Dekker Inc.: New York, **1996**.
24. FREUNDLICH H. M. F. Over the adsorption in solution. *J. Phys. Chem.* **57**, 385, **1906**.
25. LANGMUIR I. The constitution and fundamental properties of solids and liquids. *J. Am. Chem. Soc.* **38**, 2221, **1916**.
26. DUBININ M. M. The potential theory of adsorption of gases and vapors for adsorbents with energetically nonuniform surface. *Chem. Rev.* **60**, 235, **1960**.
27. NOWAK-WINIARSKA K., WROBEL S., SIENKIEWICZ-CHOLEWA U. Application of sequential analysis with the BCR method in the estimation of effects of chemical remediation of soil polluted with copper. *Chem. Spec. Bioavailab.* **24**, 53, **2012**.
28. SUTHERLAND R. A., TACK F. M. G. Fractionation of Cu, Pb and Zn in certified reference soils SRM 2710 and SRM 2711 using the optimized BCR sequential extraction procedure. *Adv. Environ. Res.* **8**, 37, **2003**.
29. SUTHERLAND R. A., TACK F. M. G. Determination of Al, Cu, Fe, Mn, Pb and Zn in certified reference materials using the optimized BCR sequential extraction procedure. *Anal. Chim. Acta.* **454**, 249, **2002**.
30. TAKENO N. Atlas of Eh-pH diagrams: intercomparison of thermodynamic databases. National Institute of Advanced Industrial Science And Technology. Research Center for Deep Geological Environments. Geological Survey of Japan Open File Report. **419**, pp.85-87, **2005**.
31. GHOBARKAR H., SCHAF O., GUTH U. Zeolites—from kitchen to space. *Prog. Solid State Chem.* **27**, 29, **1999**.
32. JANSEN J. C. in: VAN BEKKUM H., FLANIGEN E. M., JACOBS P. A., JANSEN J. C. (Eds.). Introduction to zeolite science and practice, 2<sup>nd</sup> ed.; Elsevier: Amsterdam, pp. 13-39, **2001**.
33. NIBOU D., MEKATEL H., AMOKRANE S., BARKAT M., TRARI M. Adsorption of Zn<sup>2+</sup> ions onto NaA and NaX zeolites: kinetic, equilibrium and thermodynamic studies. *J. Hazard. Mater.* **173**, 637, **2010**.
34. SVILOVIĆ S., RUŠIĆ D., ŽANETIĆ R. Thermodynamics and adsorption isotherms of copper ions removal from solutions using synthetic zeolite X. *Chem. Biochem. Eng. Q.* **22**, 299, **2008**.
35. BALINTOVA M., HOLUB M., SINGOVSKA E. Study of iron, copper and zinc removal from acidic solutions by sorption. *Chem. Eng. Trans.* **28**, 175, **2012**.

