

SORPTION OF HEAVY METAL IONS FROM AQUEOUS SOLUTION BY GLAUCONITE

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ABSTRACT

In the present paper the results of heavy metals sorption on glauconite were presented in terms of their initial concentration, contact time, ionic strength and pH of the solutions. A better match of the results of sorption was found for adsorption isotherms according to the Langmuir equation. Glauconite manifested the highest sorption capacity towards lead ions-9.12 mg/g, lower towards Cd(II)-3.44 mg/g and the lowest towards Zn(II)-3.07 mg/g and Cu(II)-2.96 mg/g. After the heavy metal sorption, a regeneration of glauconite and further sorption are possible. The highest regeneration equaled 80% with the initial concentration of 5 mg/L. With the increase of the concentration it decreased to 56%. In further regeneration cycles, desorption and sorption decreased proportionally by 2-3%. The optimum contact time to obtain the equilibrium state amounted to 180 minutes. The pseudo-second-order equation adjusts very well the experimental data, as it can be noted by the high correlation coefficients, and close values of sorption capacity calculated on the basis of the equation of pseudo-second-order to the values obtained experimentally. In the metal solutions of pH=2, pH=4, pH=6 and with a variable NaClO₄ electrolyte concentration in the range of 0.00-0.05 M, there was a significant decrease in sorption compared to the solution without electrolytes. The heavy metal removal efficiency increased with the increase in pH of the stock solution. The highest sorption of Pb(II) ions was reached at pH=6.3, Cu(II) at pH=7.2, Zn(II) pH=7.6 when it comes to ions of Cd(II) it was reached at pH equal to 9.

KEYWORDS:

glauconite, heavy metals, sorption isotherms, kinetics

1. INTRODUCTION

Heavy metals have a high potential risk for the biological environment and for humans. Wastewater from industries contains some of these toxic metals. For the treatment

of industrial wastewater containing heavy metals physico-chemical methods are used [1-10]. However, these techniques may involve high costs and results in toxic derivatives. In the last few years, sorption methods have been shown as an alternative method for removing dissolved metal ions from liquid waste [11].

Sorption of heavy metals on clay surfaces is important for economic reasons because most natural clays are low-cost and readily available. Glauconite is one of them. This mineral has been widely used for geochronological analysis [12-14] and for the removal of radionuclides [15-17]. Pioneering works on sorption on glauconite have appeared about 30 years ago [18, 19]. Further studies have shown that glauconite effectively removes lead, zinc and cadmium ions in static conditions [20]. A similar sorption study was obtained for the Lithuanian glauconite [21]. The removal of zinc, copper and cadmium ions from aqueous solutions [22-24] and mine water [25-26], as well as removal of copper ions from waste water from the PCB production [27], laundry waste and landfill leachate [28], have positive results. Moreover, the removal of As(V) depending on the initial concentration, contact time and the pH of metal solution was examined under static conditions [29].

With the use of activated tertiary glauconite from Lublin, a high degree of heavy metals removal and rapeseed oil bleaching from β -carotene were obtained [30].

Glauconite from Lublin is classified as a low-cost natural material. This claim is substantiated by its availability at the surface deposition in tertiary sediments. Due to its petrographic form, the concentrates of this mineral may be easily obtained using simple technological processing methods. The result is an easy and inexpensive sourcing of regional heavy metal sorbent.

2. MATERIALS AND METHODS

2.1 Characterization of glauconite

A clay mineral taken from a borehole in the footwall of mining working from the construction sand mining "Nowodwór I" constituted the object of the research. Glauconite occurs mainly in tertiary sediments of quartz sand and silts, which are related to the sedimentation of the Upper Paleogene (Eocene and Oligocene). These deposits

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transgressively underlie on marls and mudstone of the upper Maastrichtian.

The examined mineral was separated magnetically from quartz sand with the use of neodymium and samarium magnet. Then, it was sieved into different grain size fractions: <63 μm , 63-125 μm , 125-250 μm , 250-500 μm , 500-800 μm , >800 μm . The size fraction (125-500 μm) was used for further testing. Furthermore, grains of quartz containing magnetic inclusions derived from magnetite were selected and discarded in a separate fraction in binocular magnifying glass images. In this way a monomineral concentrate of glauconite was obtained.

Physical properties of glauconite were determined on the basis of appropriate standards [31-33]. Cation-exchange capacity of glauconite was identified by the amount of Ba^{2+} ions in the saturated sample and desorbed by 1M MgCl_2 . This method is recommended by the international organization APIPEA (Association Internationale pour l'Etude des Argiles), which deals with clay minerals [34, 35] and is widely described in literature [36-38].

Point of zero charge for glauconite was determined using potentiometric titration method [39, 40]. Experiment was performed in a continuously-stirred reaction vessel containing distilled water, electrolyte and immersed in a water jacket to control the temperature. 0.5 g of dried sample was suspended in 50 ml of solution continuously purged with pure N_2 gas. Acid and base additions were controlled using a 702 SM Titrino (Metrohm) autotitrator and pH measured. Titrations were conducted at 0.1, 0.01 and 0.001 M ionic strength using NaClO_4 as the background electrolyte both with and without glauconite sample present.

The morphological characteristic of the main mineral components as well as the examination of chemical composition in the microsite were conducted with the use of a scanning electron microscope (SEM)-Quanta FEG 200 equipped with a system of chemical composition analysis based on the energy dispersive X-Ray-EDS of EDAX company.

2.2 Sorption experiments

Sorption measurement was made with the use of a batch technique at room temperature. A stock solution of each metal was prepared by dissolving an appropriate amount of $\text{Pb}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in distilled water, respectively. The concentrations of metals in solutions, before and after sorption, were determined with the use of atomic absorption spectroscopy (AAS) performed on the spectrometer Philips PU-9100X. The pH of stock solution was modified with the use of 0.1 M HCl and 0.1 M NaOH and measured with Orbeco-Hellige pH meter. In each batch experiment the samples were shaken at 25°C at 150 rpm for 24 h, and centrifuged at 10000 rpm for 10 minutes. After that, the concentration of metals (C_e) and pH were marked in the solution.

When it comes to the influence of initial concentration on sorption, metal solution concentration varied from

5 to 220 mg/L, pH=4, and the glauconite amount was 1.0 \pm 0.01 g.

The sorption of heavy metals on glauconite was also studied in terms of the influence of time when it comes to the contact between minerals and solutions. Initial concentration (C_0) of Cd(II) solution was 51.1 mg/L, Cu(II)-50.4 mg/L, Zn(II)-51.3 mg/L, Pb(II)-48.7 mg/L. 450 mL of the stock solutions of heavy metal ions (pH=4) were shaken with 4.5 g of glauconite for different intervals of time ranging from 5 to 2880 minutes and then centrifuged.

The influence of pH in the range of 2-12 was studied while the concentrations of metals solutions were 51 mg/L, the volume of solutions was 40 mL, the shaking time 24 h and the amount of glauconite was 0.5 g.

In order to investigate the influence of the ionic strength, 100 mg of glauconite samples were successively placed in the polypropylene tubes and filled with 5 mL of solution with varied concentration of NaClO_4 (0.000-0.001-0.01-0.05 M) and the initial pH (2.0, 4.0, 6.0). Metals solutions concentrations that were used in the study were 51 mg/L.

Desorption was conducted after the sorption of heavy metals from solutions with different initial concentrations of 5-220 mg/L. In the desorption study, after reaction with metal solutions, glauconite samples were washed twice with the use of sorbent suspension shaken for 15 minutes, with 5 mL of distilled water again and centrifuged. After washing, there were no heavy metals washed in water. The concentration of metals (C_e) was determined after drying them to air-dry state. Furthermore, they were filled with 5 mL of desorbing solution-1 M NH_4Cl after 24 h of shaking and centrifugation.

The value of desorption was defined as a percentage of the tested, desorbed substance for the absorbed heavy metals:

$$D\% = (m_{des}/m_{ads}) \cdot 100$$

where:

m_{des} – stands for the mass of the substance desorbed in time (mg),

m_{ads} – stands for the mass of substance sorbed by glauconite in equilibrium sorption (mg).

Then, in order to determine the possibility to reuse the mineral after regeneration cycles, the sorption of heavy metals by mineral was performed three times (sorption/desorption). For this purpose, only solutions with a concentration of heavy metals that equaled $C_0=50$ mg/L were used in the experiment, and the sample weight was 1.0 \pm 0.01 g.

2.3 Analyzing sorption data

The term “sorption” usually defines the change in concentrations of chemical constituents in the solid phase as a result of mass transfer between solution and solid. Therefore, sorption includes various types of removal mechanisms such as an adsorption and ion exchange [41]. In the present study the word “sorption” used can include both

adsorption and precipitation. The concentration of heavy metals in the solid phase q_e (mg/g) was determined by analyzing the corresponding heavy metal concentration before and after the treatment. The following equation was used to conduct the analysis:

$$q_e = \frac{(C_0 - C_e)V}{W}$$

where:

C_0 i C_e stands for the initial and equilibrium heavy metal concentrations in the solution (mg/L),

V - volume (L),

W - is the weight of the sorbent (g).

The definition of percent removal is as follows:

$$\% \text{ removal} = \left(\frac{C_0 - C_e}{C_0} \right) 100$$

In order to perform the mathematical description of sorption, isotherms were used. They check the consistency of the results with the values predicted by the models of Langmuir [42] and Freundlich [43].

The Langmuir model describes sorption on homogeneous surface, that is energetically homogeneous, where the localized sorption takes place. There was a sorption layer that was formed on the sorbent surface, also called monolayer. It did not include the change in energy caused by the covering of the sorbent surface and chemical interactions between the different molecules of sorbate [44].

The Langmuir equation has the following form:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$$

where:

C_e – the equilibrium concentration of metal ions in solution (mg/L),

q_e – the number of the metal ion sorbed by sorbent mass unit (mg/g),

q_m – the maximum amount of ions covering the surface of the sorbent (monolayer capacity) (mg/g),

K_L – the Langmuir adsorption constant, characteristics of particular system (L/mg).

The essential characteristics of the Langmuir isotherm can be characterized by a separation factor or equilibrium constant K_R [45], which is defined as:

$$K_R = \frac{1}{1 + K_L C_0}$$

where:

K_R – dimensionless separation factor,

C_0 – initial concentration of heavy metal in the solution, (mg/L),

K_L - Langmuir constant (L/mg).

Taking into consideration the criteria given below, the separation factor K_R indicates the isotherm shape and

whether the adsorption is favorable ($0 < K_R < 1$) or not ($K_R > 1$). Where $K_R=0$ the type of isotherm is irreversible, $K_R=1$ -linear [46].

The Freundlich equation is an empirical relationship according to which it is assumed that the energy sorption of a metal binding to a site on a sorbent depends on whether the adjacent sites are already occupied or not [43]. This empirical equation has the following form:

$$q_e = K_F (C_e)^{\frac{1}{n}}$$

where: K_F is correlated with the quantity of sorbate associated with the sorbent, and n is the Freundlich isotherm constant related to the strength of the sorption. The Freundlich exponent, n , should have values within the range of 1 to 10 for classification for favorable sorption [47].

2.4 Kinetics model

The rate of sorption capacity saturation described the equations of kinetics that related the rate of the process (dq_t/dt) as functional relationship with the concentration of heavy metals in the solid phase ($q_e - q_t$). In order to analyze the rate of heavy metal sorption on glauconite, pseudo-first-order and pseudo-second-order equations were used. In the model of pseudo-first-order, the rate of the reaction is directly proportional to the difference in the equilibrium concentration of the sorbate in the solid phase of sorbent and to the instantaneous concentration of the solid phase [48]. This model is illustrated by the following equation:

$$\frac{dq_t}{dt} = k_1 (q_e - q_t)$$

where q_t - the amount of sorbed ions after time, based on the unit of the sorbent weight under non-equilibrium conditions [mg/g], q_e - the amount of ions sorbed in equilibrium, k_1 - Lagergren constant, also called the rate constant of pseudo-first-order sorption [1/min].

For the presentation of experimental data, the Lagergren linear equation was used:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t$$

Pseudo-second-order kinetics model assumes that the rate of the process is proportional to the square of the difference of the equilibrium concentration of the sorbate in the solid phase and the instantaneous concentration in the solid phase of sorbent [49]:

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

where: k_2 – the rate constant of pseudo-second-order sorption.

The linearized form used to determine the model parameters of pseudo-second-order may be presented with the use of several equations, one of which the most commonly used is:

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

These relations allow for the estimation of the model sorbate concentration on the surface of solid sorbent and fixed rates of sorbent saturation capacity (k_1 and k_2). If the curves are arranged in a straight line then the appropriate process of saturation of the deposit (first or second) is determined and confirmed. Linear regression for both models allows for the determination of both the model of concentration of metal ions on the sorbent surface and the values of the fixed rates of the process (k_1 , k_2).

3. RESULTS AND DISCUSSION

3.1 Characterization of glauconite

Glauconite is a clay mineral that is common in tertiary sediments of the Lublin Region. The characteristics of X-ray diffraction of glauconite revealed that it represents well-ordered structure. The type of its packets is ISII. Moreover, they have high potassium content and swelling packages in the range of 5-15%, which place the tested glauconite to the polytype 1M [50].

According to sieve analysis, the grain size fractions 63-125 μm , 125-250 μm and 250-500 μm constituted 22%, 23% and 36%, respectively of the total weighted mass of the sample. Slightly smaller amount was constituted for size fraction 500-800 μm that was 18%, while fraction 800-1000 μm constituted 3% of the total weighted mass of the sample. Uniformity coefficient was smaller than 5 ($C_u=3.70$), which means that glauconite is a mineral that has equal size of grains. Glauconite grains with a diameter of 125-500 μm were selected to the research because they constituted about 60% of the total mass of glauconite. The resulting filtration coefficient corresponds to the approximate values for medium-grained sands. The bulk density of the mineral equals 1.39 g/cm^3 , whereas specific density is 2.75 g/cm^3 . Glauconite physical parameters are shown in Table 1.

TABLE 1 - Physical parameters of glauconite

Physical properties		Glauconite
Filtration coefficient	[cm/s]	$2.6 \cdot 10^{-3}$
Bulk density	[g/cm ³]	1.39
Specific density	[g/cm ³]	2.75
Ion-exchange capacity	[mval/g]	0.17

Glauconite ion-exchange capacity determined with the use of barium chloride method was 0.17 mval/g of the mineral.

It represents spherical morphological changes of grains with the size of about 180 μm (Figure 1). The vast majority of glauconite grains have smooth, often cracked surfaces. A detailed analysis of the morphology of glauconite grains performed with the use of scanning electron microscopy revealed its fine-crystalline nature (Figure 2). With 15000X magnification, in cracked grains irregularly arranged frame aggregates of glauconite can be observed (Figure 3), sometimes turning into enamels.

On the basis of the quantitative analysis of chemical composition of microsite, it was stated that the percentage content of oxides is the following:

SiO₂–57.42%, Fe₂O₃–23.3%, K₂O–7.80%, Al₂O₃–6.9%, MgO–4.17%, CaO–0.5%.

3.2 Effect of initial metal concentration

The effect of initial concentration on the sorption of Pb(II), Cu(II), Zn(II), and Cd(II) ions was carried out with the concentrations of 5, 10, 20, 50, 100 and 220 mg/L. Results for the sorption of heavy metals on glauconite, that is the percentage ratio of the amount sorbed to the initial concentration of metal in the solution, are presented in Figure 4. Metal removal efficiency decreased with the increase of initial metal concentration.

The highest lead sorption efficiency at a level of 100% was observed at the concentration of the initial solution equaled 5, 10 and 20 mg/L. A further increase in the initial concentration of the lead solution led to a decrease in the

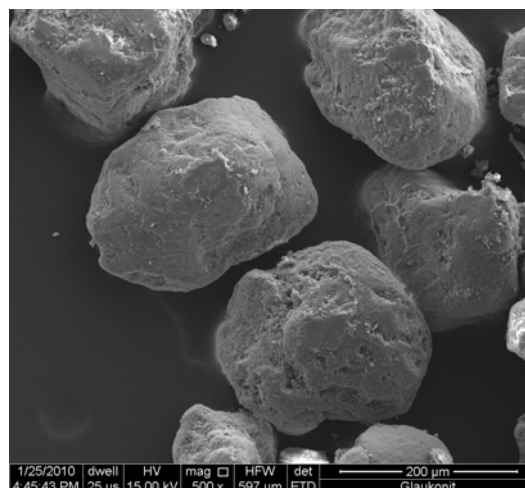


FIGURE 1 - Morphological changes of glauconite aggregates, SEM, 500X magnification



FIGURE 2 - Glauconite aggregate of round shape, SEM, 200X magnification

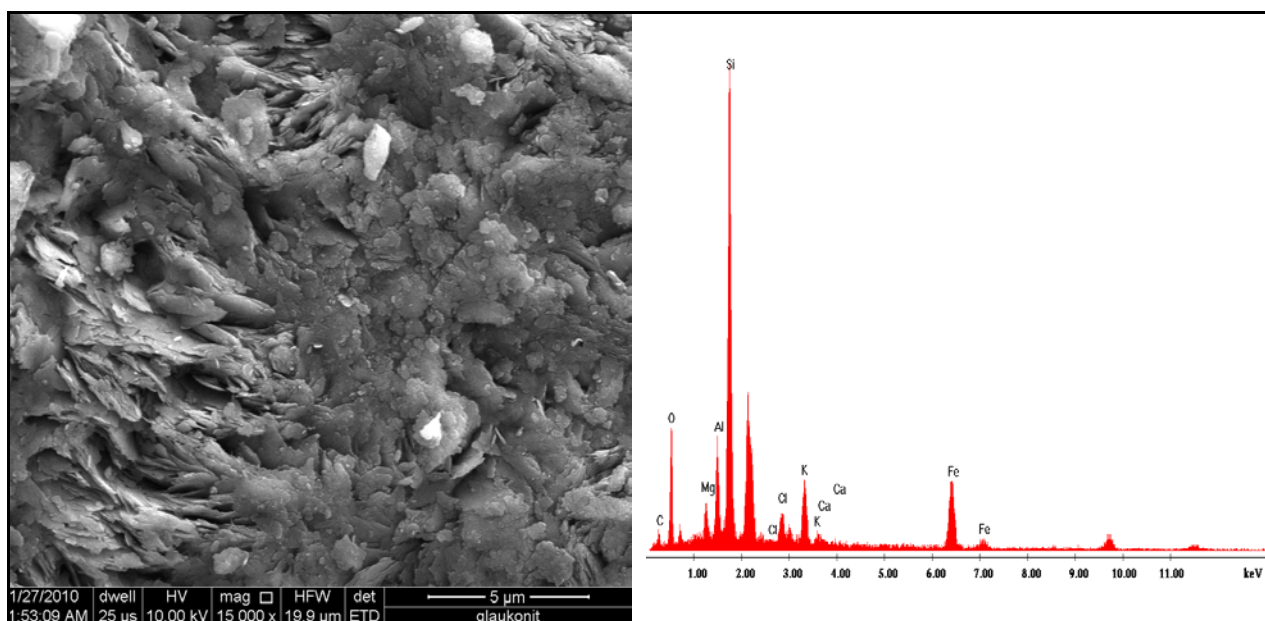


FIGURE 3 - Scaled grains of glauconite (SEM, 15000X magnification) and its spectrum of the chemical composition in microsite (SEM-EDS)

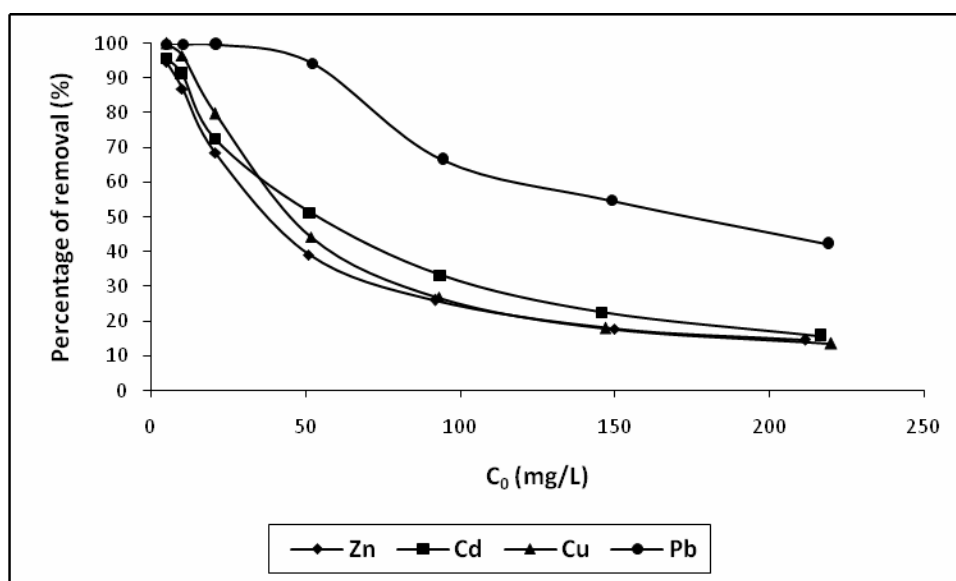


FIGURE 4 - Effect of initial metal concentration on percent removal of heavy metals by glauconite

sorption efficiency to 42%. At a concentration of the copper solution of 5 mg/L the sorption capacity was also 100%. Slightly lower sorption efficiency was observed during the removal of cadmium ions, where with the initial concentration of 5 mg/L the sorption efficiency was 96%, while in case of zinc ions removal was 95%. A further increase in concentrations to a value of 50 mg/L caused a decrease in the sorption capacity and at a concentration of 220 mg/L it was 13% for Cu(II), 14% Zn(II), and 15% for Cd(II). Removal efficiency of heavy metals by glauconite decreased with the increase of their solution concentration. It was explained by the limited number of active places on the surface of the sorbent.

The glauconite examined by scientists from Devon in the United Kingdom was more effective in terms of the removal of heavy metals from aqueous solutions. In neutral solution, and the initial metals concentration of about 50 mg/L, there was about 99% of Cu(II) ions and 90% of Zn(II) and Cd(II) removed from aqueous solutions [22, 27]. In the Lublin Region, in the same conditions, there were 44% of Cu(II), 39% Zn(II), 51% of Cd(II) removed with the use of glauconite.

The results indicated that the initial concentrations in the range from 5 to 20 mg/L metal selectivity is the following: Pb(II) > Cu(II) > Cd(II) > Zn(II). The percentage

removal of heavy metal ions seemed to be inversely proportional to the hydrated ionic radii of them: Pb(II)-4.01 Å > Cu(II)-4.19 Å > Cd(II)-4.26 Å > Zn(II)-4.30 Å [51, 52]. At the higher concentrations (50-220 mg/L) metal selectivity has changed. Copper ions were sorbed in the smallest amounts, and cadmium and zinc ions in bigger amounts. Sorption was directly proportional to the molecular weight and ionic radii of metals: Pb(II)-1.19 Å > Cd(II)-0.95 Å > Zn(II)-0.74 Å > Cu(II)-0.71 Å [52-54].

In the case of equal par ions, hydrodynamic radius is the most important aspect. With the increase of atomic mass of heavy metal ions, their hydrodynamic radius decreased. It means that their interchangeable energy increases the energy input to glauconite. Lead ions have the highest molecular weight, and therefore have a particular connection to the structure of glauconite.

Glauconite from tertiary sediments of the Lublin Region, similarly to glauconite from Cretaceous age in Jonava [21] and glauconite from Annie Arundel County, Maryland, USA [20], removed lead in the most effective way. In quoted works, cadmium and zinc also showed variable positions in the sequence of selectivity.

The sorption isotherms, including the Langmuir and Freundlich isotherms, were applied to the equilibrium data to describe the main interactive mechanisms involved in the removal process. The values of constant equations of the Langmuir and Freundlich isotherms were adjusted to the experimental data. Linearization of the Langmuir and Freundlich equations allowed to determine the sorption parameters and the correlation coefficients, shown in Table 2. On the basis of Figure 5, the relation between the experimental data and isotherms was designated theoretically with the use of linear regression. On the basis of the correlation coefficients R^2 , it was assumed that the experimental data were well adjusted to both isotherms. However, undoubtedly better match of the results of heavy metals sorption were found for adsorption isotherms according to the Langmuir equation on the basis of the correlation coefficient R^2 ($R^2 \sim 1$).

The isotherm constants showed the calculated Freundlich parameters K_F and n , which indicated favorable sorption. The values of Langmuir constant K_L for sorption of heavy metals by glauconite increased from 0.117 to 0.309, confirming favorable sorption under the experimental conditions of the study (Table 2).

The maximum sorption capacities q_m (mg/g) calculated from Langmuir were in most cases comparable with

experimental values. Glauconite manifests the highest sorption capacity for lead ions-9.12 mg/g, lower for Cd(II)-3.44 mg/g and the lowest for Zn(II)-3.07 mg/g and Cu(II)-2.96 mg/g.

Comparison of the sorption capacity of glauconite and other sorbents for the heavy metals, such as Pb(II), Cd(II), Zn(II), Cu(II) is presented in Table 3.

The literature data [21, 47, 55-64] show that in the similar conditions of sorption process of heavy metals, the sorption capacity of glauconite is comparable to some of clay minerals, and sometimes it may be even higher.

3.3 Desorption study

The desorption process was performed to determine the stability of the relation between heavy metals and clay mineral. Ion exchange processes have a relatively weak influence on relation of heavy metals with a mineral surface. They have also an effect on easy recovery and further application of the material. The presented research indicated that regardless of the initial concentration of heavy metals in solutions, total desorption was not possible. Therefore, heavy metals are adsorbed from solutions in an exchangeable and a nonremovable form in the entire concentration range.

The dependence of desorption value (1 cycle) on the initial concentration of heavy metals solutions are presented in Figure 6.

On the basis of the research, it was found that at the lowest concentrations of heavy metals sorbed on glauconite have an easily removable form (Figure 6). After sorption of heavy metals from solutions with the initial concentration of 5 mg/L the most easily desorbed was Cu(II)-80%, followed by Zn(II)-79%, Cd(II)-75% and Pb(II)-74%. With the increase of stock solution concentration, the percentage level of metals removal gradually decreased. In the case of Pb(II) desorption decreased to 48%, of Cu(II)-56% and of Zn(II) to 61%. Cd(II) ion desorption reached 74% almost in the whole range of initial concentrations, and with the concentration of 220 mg/L decreased to 70%. In the whole range of initial concentrations, lead was the most strongly bound to the surface of the mineral. When it comes to cadmium ions, they are desorbed in the greatest amounts, which lead to a larger share of ion-exchange processes. The research revealed that the desorption was between 56-80% in the whole range of initial concentrations.

TABLE 2 - The values of parameters for Langmuir and Freundlich isotherms used in this study

Element	Langmuir				Freundlich		
	q_m (mg/g)	K_L (L/mg)	K_R	R^2	1/n	K_F (L/g)	R^2
Cd(II)	3.44	0.207	0.022	0.999	0.292	0.870	0.973
Cu(II)	2.96	0.213	0.021	0.995	0.172	1.231	0.996
Zn(II)	3.07	0.117	0.039	0.989	0.278	0.758	0.989
Pb(II)	9.12	0.309	0.015	0.986	0.242	3.103	0.963

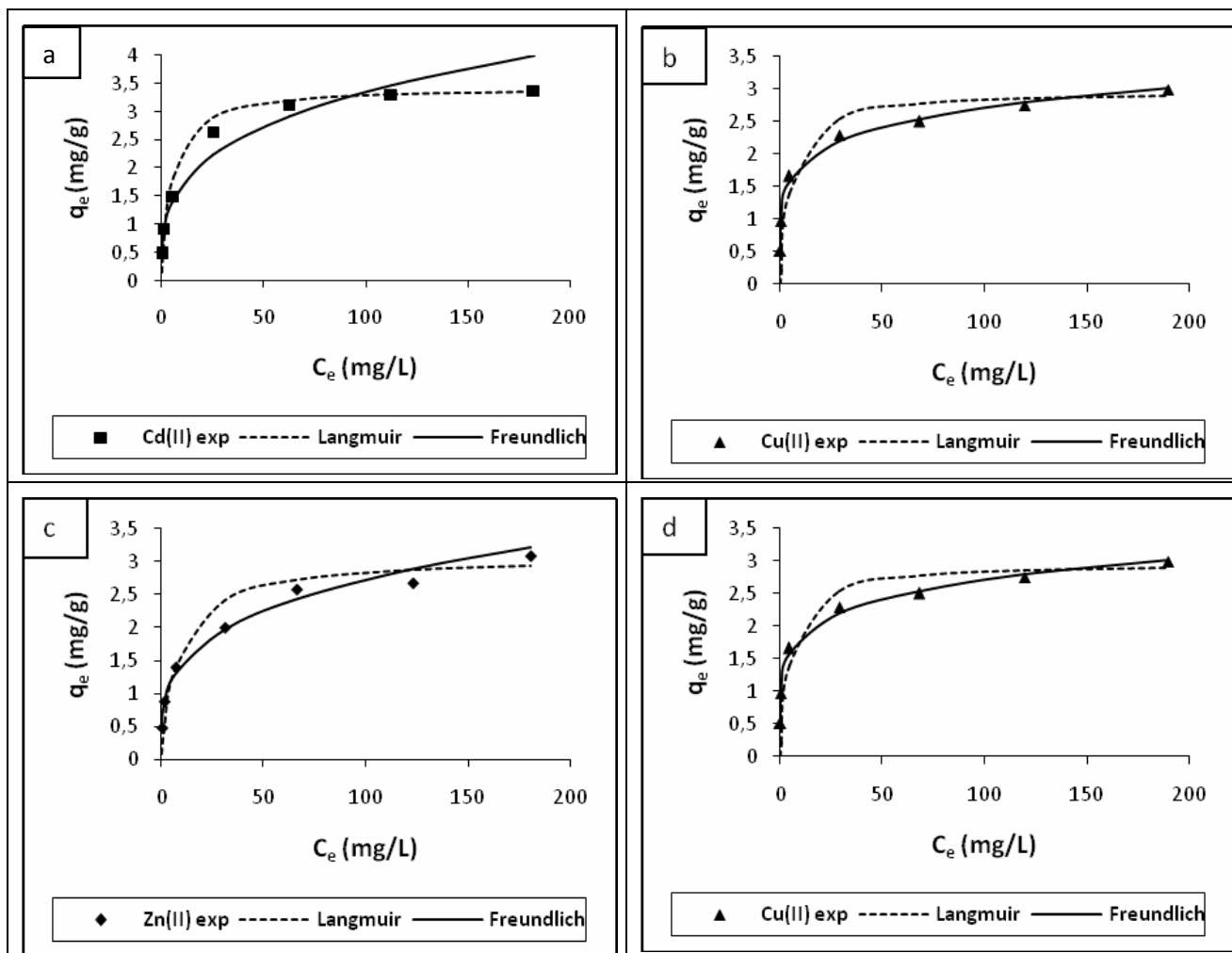


FIGURE 5 - Adsorption isotherms and Langmuir and Freundlich fitting for a) Cd(II), b) Cu(II), c) Zn(II), d) Pb(II) sorption on glauconite

TABLE 3 - Comparison of the sorption capacity of glauconite with other sorbents

Sorbent	Pb(II)	Cd(II)	Zn(II)	Cu(II)	Reference
Glauconite	9.12	3.44	3.07	2.96	This study
Kaolinite	2.35	0.88	-	1.22	[55]
Kaolinite	-	3.04	-	4.47	[56]
Kaolinite	-	3.7	-	1.9	[57]
Kaolinite	-	0.75	1.8	0.76	[47]
Kaolinite	11.5	6.8	-	-	[58]
Turkish siderite	10.32	-	-	-	[59]
Low rank Turkish coals	-	-	1.2	1.62	[60]
Montmorillonite	-	-	-	7.16	[61]
Natural zeolite	-	-	5.38	3.37	[62]
Clinoptilolite	1.6	2.4	0.5	1.64	[63]
Clinoptilolite	6.00	3.7	2.7	3.8	[64]
Glauconite	10.5	4.1	1.37	-	[21]

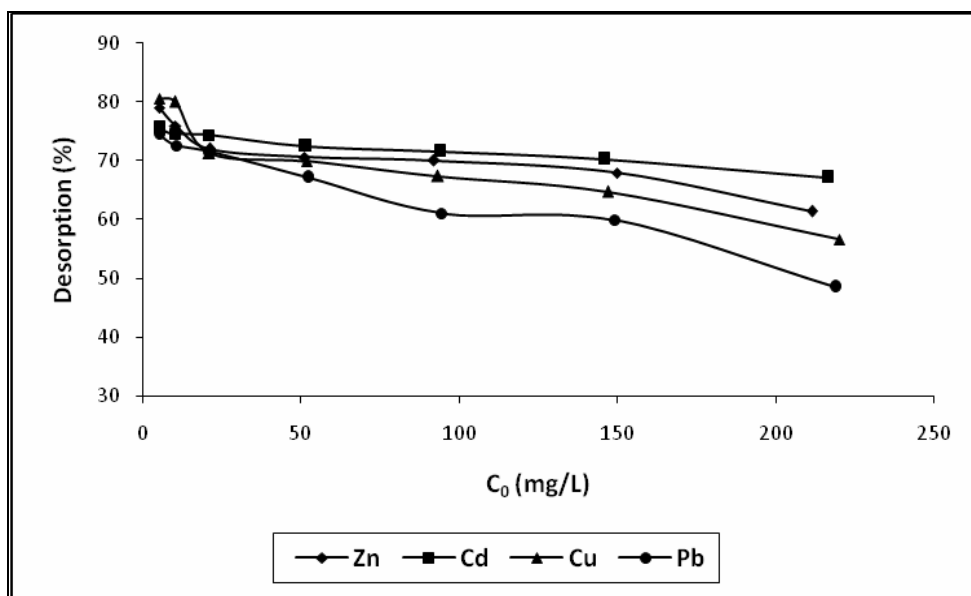


FIGURE 6 - Desorption of heavy metals ions by glauconite in accordance with their initial concentration (1 cycle)

TABLE 4 - Sorption-desorption cycles for heavy metal ions

Element	I cycle		II cycle		III cycle		IV cycle	
	Des. %	Ads. (mg/g)	Des. %	Ads. (mg/g)	Des. %	Ads. (mg/g)	Des. %	Ads. (mg/g)
Pb(II)	67	3.27	65.70	3.18	61.82	3.02	59.4	2.83
Cu(II)	69	1.58	67.50	1.52	65.54	1.45	63.6	1.38
Zn(II)	70	1.39	68.30	1.33	66.81	1.29	63.9	1.22
Cd(II)	72	1.89	70.50	1.81	67.90	1.72	65.2	1.63

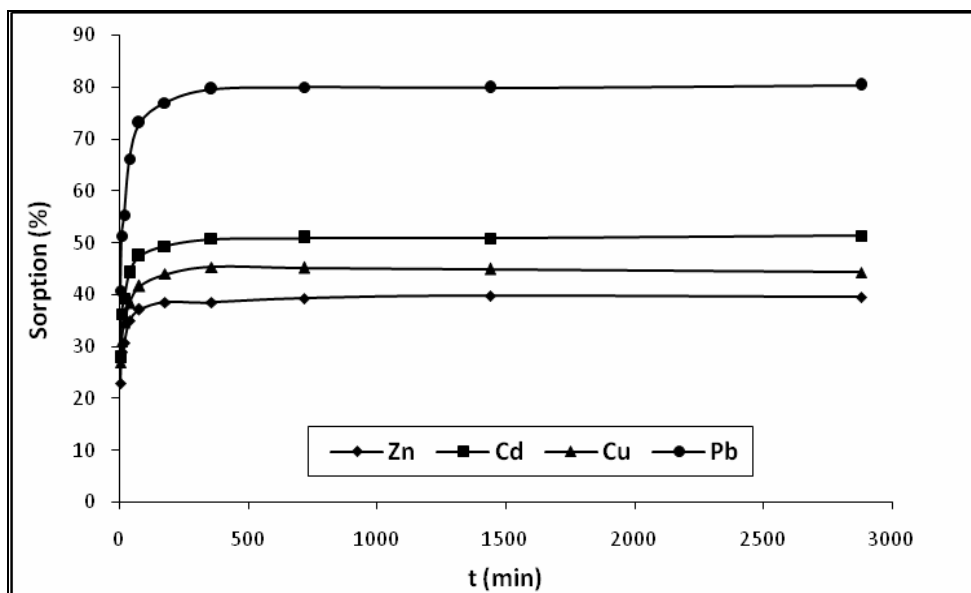


FIGURE 7 - Effect of contact time for the sorption of heavy metals by glauconite

The ability to reuse the regenerated glauconite in order to remove heavy metals from aqueous solutions ($C_0=50$ mg/L) was very effective (Table 4). After the first

desorption cycle of Pb(II), Cu(II), Zn(II) and Cd(II) ions; which were 67, 69, 70 and 72%, respectively; the subsequent sorption of heavy metals was lower. The value of

the sorption capacity was reduced to 3.27 mg/g for Pb(II), 1.58 mg/g for Cu(II) 1.39 mg/g-Zn(II) and 1.89 mg/g for Cd(II).

Desorption of heavy metals in subsequent cycles was reduced by 2-3%. Thus, the sorption capacity of mineral was being slightly reduced.

3.4 Effect of contact time

Contact time is an important parameter because this factor determines the sorption kinetics of a sorbate at its given initial concentration. These results indicated that with the increase of time the removal of heavy metal ions increased to a certain point of equilibrium (Figure 7).

At the initial stage the process goes fast because the change includes those ions in the crystal lattice, which are at interchangeable positions and are readily accessible for heavy metal ions. Taking the process of metals immobilization into consideration; Pb(II), followed by Cd(II), Cu(II), Zn(II) are metals that are the most effectively sorbed on glauconite. During the first five minutes of the reaction, 41% of the total amount of Pb(II) was immobilized, 28%-Cd(II), 27%-Cu(II), and 23%-Zn(II). The state of ion equilibrium in the glauconite structure is reached after 180 minutes. At that time, 80% of Pb(II), 50% of Cd(II), 45% of Cu(II) and 39% of Zn(II) were removed by glauconite. Therefore, the analysis of kinetic curves for each of the metals could arrange them in series, due to the increasing ion exchange rate of which corresponded to the increasing atomic mass: zinc, copper, cadmium and lead. It indicated that glauconite showed stronger preference for Pb(II) than for Zn(II).

The kinetic parameters of sorption were determined with the use of models of pseudo-first and pseudo-second-order. Their comparison is presented in Table 5.

On the basis of these relations, it was found that the equation of pseudo-first-order was not applicable for the description of the kinetics of the presented sorption process due to the poor quality of adjustments to the experimental data. Therefore, there were large derogations from the linearity, especially near to the equilibrium. As for the equation of the pseudo-second-order, it adjusted very well the experimental data, as it could be noted by the high correlation coefficients close to 1, and close values of sorption capacity calculated on the basis of the equation of pseudo-second-order to the values obtained experimentally.

The rate constant k_2 , determined on the basis of pseudo-second-order model, had the highest value for the sorption of Cu(II) ions and the lowest for the sorption of Pb(II) ions.

The data clearly showed that the most appropriate kinetic model describing sorption process for heavy metals on glauconite was pseudo-second-order model.

3.5 Effect of ionic strength

The dependence of the sorption of heavy metals by glauconite with a variable NaClO₄ electrolyte concentration (0.00 M, 0.001 M, 0.01 M, 0.05 M) is presented in Figure 8. In all experiments of the sorption of heavy metals by glauconite, the pH of stock solutions was approximately 2, 4 and 6.

In all the systems analyzed, the increase of the amount of sorbed metals with the increase in pH and a decrease in the sorption of metals with the increase of concentration of NaClO₄ electrolyte solution were quite common. Significant differences in the amount of adsorbed metals were generally noticeable during the increase in the concentration to 0.05 M NaClO₄, regardless of pH.

At pH 2.0, the change of the amount of adsorbed ions Cu(II), with increasing electrolyte concentration to 0.05 M, did not exceed 4%. At pH 4, there was a decrease in sorption from 32% to 27% observed, together with an increase in the electrolyte concentration to 0.01 M.

When it comes to the concentration of 0.05 M, there was a clear decrease in the copper sorption from 31% (0.00 M) and 22% (0.05 M) observed. A similar relation appeared at pH=6. With an increase in the electrolyte concentration from 0.00 M to 0.01 M, a decrease in the size of the sorption of 3% from the value of 47% to 44% was observed. What is more, the increase in the ion concentration of 0.05 M NaClO₄ was accompanied by a decrease in sorption to 38%.

In the case of cadmium ions removal, proportional decrease in the sorption volume with the increase in the electrolyte concentration from 0.00 M to 0.01 M NaClO₄ in the entire pH range was noted. Moreover, a significant decrease in sorption was observed at an ionic strength of 0.05 M NaClO₄. At pH=2 the increase in ionic electrolyte (0.05 M) caused a decrease in the amount of adsorbed cadmium from 13% to 7%. At pH=4 the increase in the electrolyte concentration up to 0.01 M caused a decrease

TABLE 5 - Kinetic parameters of the sorption of Zn(II), Cd(II), Cu(II), Pb(II) on natural glauconite with the use of models of pseudo-first and pseudo-second-order

Element	Measured	Pseudo-First-Order Model			Pseudo-Second-Order Model		
	$q_{e \text{ exp}}$ (mg/g)	$q_{e \text{ calculated}}$	k_1	R^2	$q_{e \text{ calculated}}$	k_2	R^2
Zn(II)	2.04	0.37	0.004	0.753	2.03	0.100	1.000
Cd(II)	2.62	0.36	0.003	0.619	2.63	0.061	1.000
Cu(II)	2.30	0.71	0.012	0.985	2.25	2.251	0.999
Pb(II)	3.92	0.62	0.003	0.626	3.92	0.035	1.000

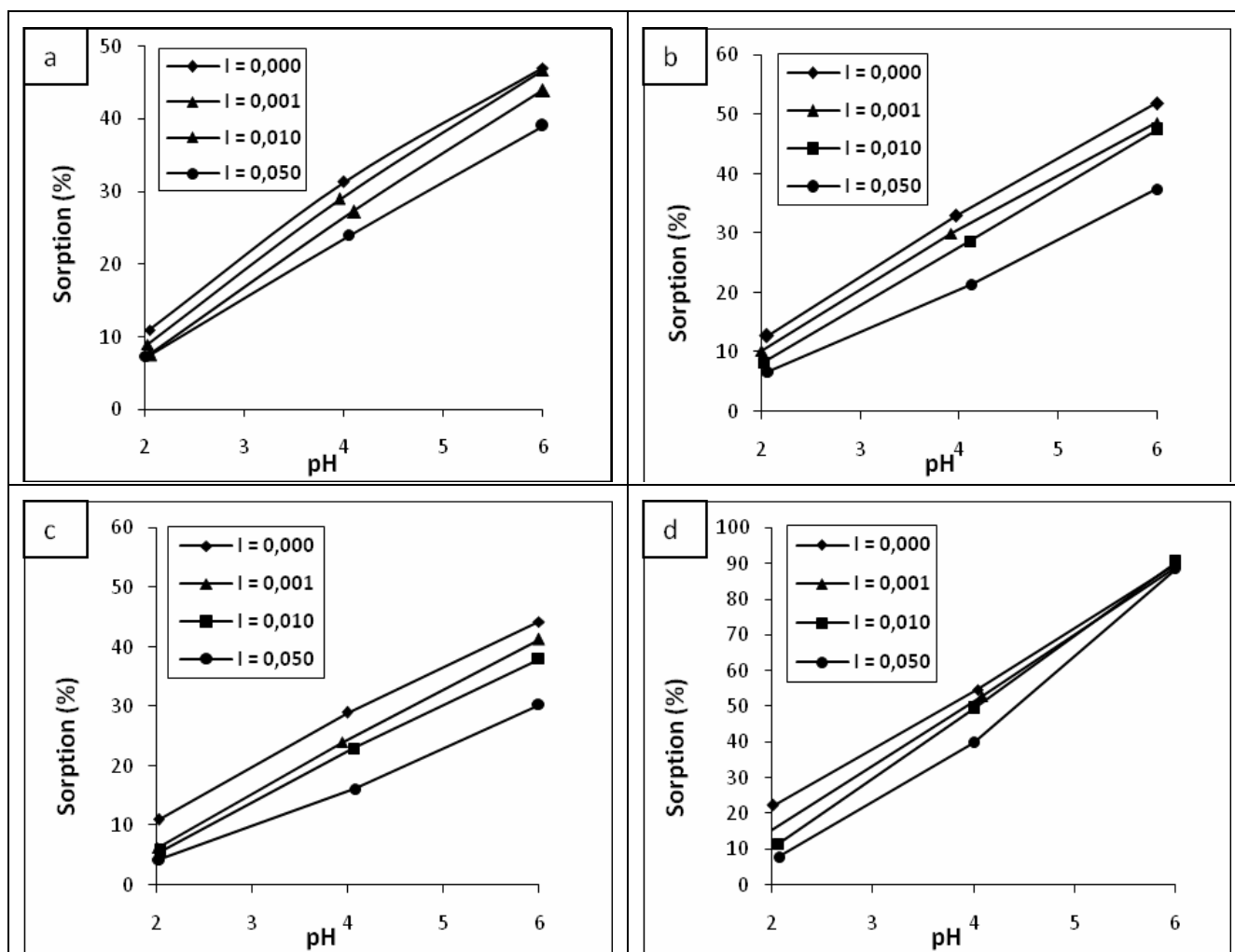


FIGURE 8 - Role of ionic strength on a) Cd(II), b) Cu(II), c) Zn(II), d) Pb(II) sorption on glauconite as a function of pH

in the amount of adsorbed ions Cd(II) of 4%, in the range of 32% to 28%; and at a concentration of 0.05 M the size of the sorption was 20%. A similar drop in adsorption size was observed at pH=6 and the electrolyte concentration was from 0.00 M to 0.01 M. There was a slight decrease in the electrolyte sorption of 3%, from the 51% to 48%. The clear decrease in sorption was noted at the electrolyte concentration of 0.05 M, where the amount of adsorbed ions Cd(II) was 37%.

Among all the elements analyzed, ionic adsorption had the greatest influence on the size of the sorption in case of Zn(II) ions. The influence increased with decreasing pH. At pH=2 there was a decrease by 7% of the amount of metal adsorbed, 11% of the value in the absence of electrolyte NaClO₄ and to 4% at the concentration of 0.05 M. When it comes to pH=4, the situation is similar as in other cases, there was a decrease in adsorbed amount of ions Zn(II) (30 of the value of to 21%) with increasing electrolyte concentration up to 0.01 M and a marked decrease in sorption (to 15%) at a concentration of 0.05 M. When pH was 6, there was an almost linear

decrease in zinc sorption together with the increase in ion concentration. In the absence of electrolyte, there was up to 44% adsorbed of the initial concentration of Zn(II) on glauconite, and at a concentration of 0.05 M-30%.

The influence of the ionic concentration on the size of ion sorption of Pb(II) was especially noticeable at pH=2 and pH=4. The amount of adsorbed metal changed only at a concentration of 0.05 M. At pH=2 the increase in the concentration of NaClO₄ was accompanied by a decrease in the adsorbed amount of lead by 14% from 22%, in the absence of electrolyte up to 8% with its concentration of 0.05 M. At pH=4, the growth of the electrolyte concentration to 0.01 M was accompanied by a decrease in sorption in the value of 51% to 45%, respectively. At pH=6 no significant changes in the size of the ion sorption of Pb(II) in a concentration range of 0.00-0.05 M, which was at a level of 90%, were observed. At electrolyte concentration of 0.05 M there was 88% of the initial amount of lead adsorbed.

These results showed that exist a competition between cations of the salt and metal ions for the active adsorption

sites of glauconite. The electrostatic interactions between metal ions and surface functional groups of mineral were impeded in the presence of ionic strength.

The active sorption sites of the glauconite may be blocked in the presence of electrolyte so metal ions were hindered to bind the surface of the sorbent [55].

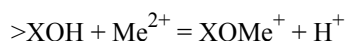
3.7 Effect of pH

The pH of the aqueous solution is an important variable in the sorption process [65, 66]. Thus, to understand the effect of pH on sorption of heavy metal ions on glauconite, pH range of 2-12 were investigated in the study. Figure 9 shows the effect of pH on sorption of Zn(II), Cd(II), Cu(II) and Pb(II) ions onto glauconite. It can be observed that the sorption percentage of heavy metals increases with an increase in pH. pH of heavy metals solutions ranging from 6 to 9 turned out to have the highest removal effectiveness.

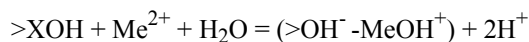
Sorption of heavy metals on clay minerals happened due to the ion exchange and surface complexation, with the contribution of ion exchange most pronounced at lower pH values [67, 68]. Furthermore, with increasing pH of a solution, resulting in the hydrolysis reaction, the precipitation of metal hydroxides takes place [21].

The participation of the above mentioned mechanisms that happen in the process of immobilization of heavy metals by glauconite depended on the pH of the solution.

Surface complex modeling is the formation of outer-sphere and inner-sphere complexes. When it comes to the inner-sphere complexes, sorbed metal ions are chemically bonded to the surface of the sorbent. Therefore, this process is also known as chemisorption or specific sorption. The mechanism of surface complexation of divalent metal cations can be presented in the following form:



In case of outer-sphere complexes, metal-ligand complexes of the type $MeOH^+$ were adsorbed. Their presence in the solution was controlled by pH. This mechanism can be illustrated in the following way:



In such case, the interactions between sorbent and sorbate were weaker than in case of inner-sphere complexes.

The symbol, $>X$ represents the surface oxide base element, in this case, typically Si, Fe, Al and Mg.

The effect of pH can be explained in terms of pH_{pzc} . The value of pH_{pzc} of studied glauconite was 6.48. Below pH_{pzc} , glauconite surface is positively charged and above pH_{pzc} is negatively charged. The origin of the positive charge is associated with the presence of basic functional groups and excessive protonation of surface below pH_{pzc} . A barrier, that was formed, consisting of the positive charge, hindered the access of the cations of heavy metals to the surface of glauconite. It resulted in a less efficient sorption at $pH < pH_{pzc}$. At higher pH values, the sorbent surface had a negative charge due to ionization of the acid groups. This leads to electrostatic attraction between the metal ions and places with negative charge on the surface of the mineral, which increased sorption. What is more, with the increase of pH, the number of hydrogen ions in solution decreased. Furthermore, the competition for heavy metal ions decreased too and the sorption was more efficient.

The gradual increase in pH leads to the formation of complex ions and precipitation of metal ions in the form of hydroxides. The loss of heavy metal ions in equilibrium solution was caused by the sorption process of cations to the surface of glauconite, the formation of complexes $MeOH^+$

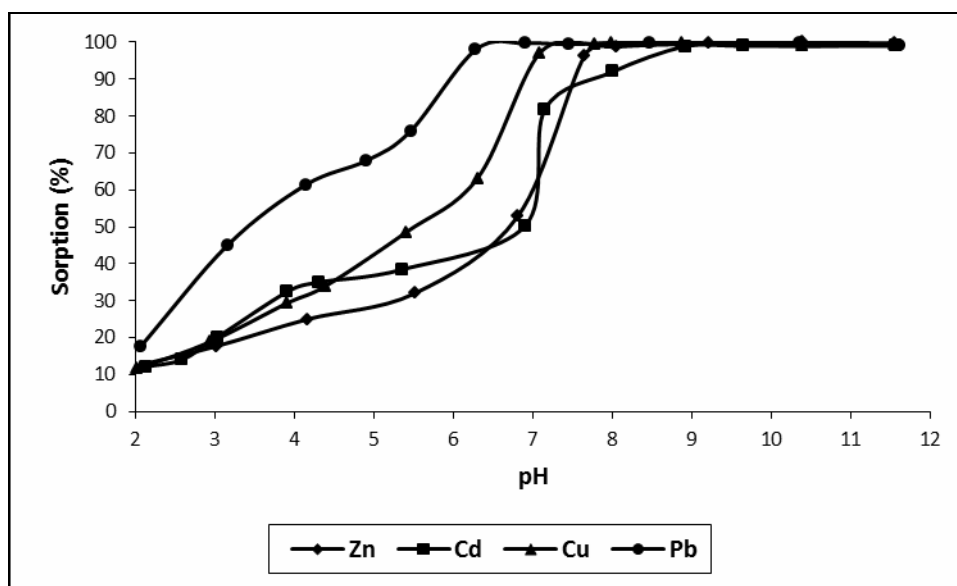
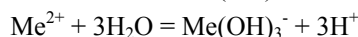
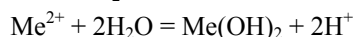
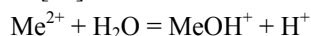


FIGURE 9 - Effect of pH on the sorption of heavy metals by glauconite

and the precipitation of hydroxides $\text{Me}(\text{OH})_2$ at higher pH values [21]:



Theoretical hydroxide precipitation pH from the values of the solubility product K_{sp} was estimated for each metal [70].

In the pH range of 2.1 to 6.9, glauconite removed from 12 to 50% of the initial amount of cadmium from the aqueous solution. The increase in pH to 7.2 resulted in a rapid loss of Cd(II) ions from an equilibrium solution (82% adsorption). It was because of $\text{pH} > \text{pH}_{\text{pzc}}$ and a negatively charged surface of glauconite. The increase in pH to 9.0 resulted in a complete immobilization of cadmium ions (sorption 100%). At high pH, there might be a hydrolysis reaction of cadmium ions and then their precipitation in the form of hydroxides. The theoretical value of the pH precipitation of cadmium hydroxide (pH above 8) may be calculated on the basis of the solubility product $K_{\text{sp}} = 7.2 \times 10^{-15}$.

In the pH range of 2 to 6.8, zinc ions were removed from the aqueous solution in an amount of 12 up to 53% of the initial amount in the solution. The increase in pH to a value of 7.65 resulted in a rapid loss of Zn(II) from the equilibrium solution (96.5% adsorption). With further increase of pH up to 8.0, zinc sorption increased up to 98.8%, and with pH above 8.0 to almost 100%. Probably a significant amount of zinc hydroxide precipitated at $\text{pH} = 7.1$, which meant that the zinc ions were removed from the solution by hydrolysis ($K_{\text{sp}} = 1.2 \times 10^{-17}$).

The lead sorption process was significant at pH 2.0-5.5. In such a scope, the sorption of lead increased from 17.5 to 77.5%, respectively. At pH amounted to 6.28 immobilization of lead ions was 98 % and above $\text{pH} = 6.9$ it exceeded 99%. It was connected with the negatively charged surface of glauconite when pH of the equilibrium solution was higher than pH_{pzc} . In higher pH a significant amount of lead hydroxide may begin to precipitate. The pH of precipitation was also theoretically calculated (around 6) in accordance with the maximum concentration of lead and the constant solubility product ($K_{\text{sp}} = 1.43 \times 10^{-20}$). Further increase in pH did not cause any change in the concentration of lead in equilibrium solution.

In the case of removing copper ions from solutions with a pH of 2.0 to 6.3, from 13 to 62 % of the initial ions was removed. The increase in pH to 7 led to the immobilization of 97% of the copper ions. Probably a significant amount of copper hydroxide $\text{Cu}(\text{OH})_2$ precipitated in pH about 5.7 which was determined on the basis of the constant solubility product ($K_{\text{sp}} = 2.2 \times 10^{-20}$).

4. CONCLUSIONS

The results indicate that glauconite from tertiary sediments in the Lublin Region effectively removes heavy

metal ions such as Pb(II), Zn(II), Cu(II) and Cd(II) from aqueous solutions. The effectiveness of sorption is influenced by the initial concentration of heavy metals, the contact time, the pH of aqueous solutions and ionic strength. Within the concentrations (50-220 mg/L) the range of heavy metal selectivity is the following $\text{Pb}(\text{II}) > \text{Cd}(\text{II}) > \text{Zn}(\text{II}) > \text{Cu}(\text{II})$. Sorption is directly proportional to the molar mass and metal ionic radii. Sorption isotherms were found to be well correlated by both the Langmuir and Freundlich model. However, better data were obtained from the Langmuir model on the basis of the correlation coefficient R^2 ($R^2 \sim 1$).

The maximum sorption capacities q_m (mg/g) calculated from Langmuir were in most cases comparable with experimental values. Glauconite manifested the highest sorption capacity for lead ions-9.12 mg/g, lower for Cd(II)-3.44 mg/g and the lowest for Zn(II)-3.07 mg/g and Cu(II)-2.96 mg/g.

Sorption equilibrium state was reached after 180 minutes. At this time, glauconite removed 80% of Pb(II), 50% of the Cd(II), 45% of Cu(II) and 39% Zn(II). Due to the appropriate adjustment of the experimental data, the kinetic of sorption is described by the pseudo-second-order model.

A significant influence of ionic strength and pH on the efficiency of sorption was observed in the study. The sorption percentage of Zn(II), Cd(II), Cu(II) and Pb(II) ions increased with the increase in pH. At $\text{pH} > \text{pH}_{\text{pzc}}$ sorption of metal cations was the most efficient in negatively charged surface of the mineral.

During the interaction between heavy metal ions and glauconite, inner layer complexes and outer layer complexes as well as ion exchange coexisted with the precipitation of the hydroxides of heavy metals. The contribution of these processes was dependent on pH of the solution. The highest sorption of Pb(II) from aqueous solutions was achieved at $\text{pH} = 6.4$, Cu(II) ions at $\text{pH} = 7.2$, Zn(II) ions at pH 8, while Cd(II) ions at $\text{pH} = 9$.

The results of the experiment on the impact of ionic strength on the sorption of heavy metals show that with an increased concentration of electrolyte solution NaClO_4 (0.0-0.5 M), the sorption of heavy metals decreases. Furthermore, it increases when the pH of the solutions is higher. The active sorption sites of the glauconite may be blocked in the presence of electrolytes, when its concentrations are higher, as a result metal ions were unable to bind to the surface of the adsorbent.

The study on desorption indicates that it is possible to regenerate and reuse minerals for the sorption of heavy metals. Desorption of heavy metals in the spectrum of initial concentrations ranged from 56 to 80%. Attempts to use the mineral after regeneration for another sorption of heavy metals were positive. Subsequent cycles of adsorption and desorption showed a similar desorption decrease by 2-3% after each cycle and a proportional decrease in sorption capacity. It allows for multiple use of glauconite in the removal of heavy metals from aqueous solutions.

ACKNOWLEDGMENTS

The study was supported by statutory funds no. S12/II/B/2013.

The authors have declared no conflict of interest.

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Received: June 20, 2013
Revised: October 30, 2013
Accepted: November 18, 2013

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