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## Application of zeolites in removal of hazardous metal ions from drilling mud wastewater

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**Abstract:** In this study, the adsorption behavior of natural and activated zeolites with respect to  $\text{Cd}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Pb}^{2+}$  and  $\text{Zn}^{2+}$ , was studied in order to consider their ability to remove hazardous metals from drilling mud. The batch method was employed, using initial metal concentrations in solution in the range of 0.1 to 2.5 mg/dm<sup>3</sup>. It was determined that independently of the concentration, the adsorption ratios of zeolite towards metal cations match the Langmuir and Freundlich isotherms. The results of the research on the reduction of concentration of hazardous metals from drilling mud wastewater by means of natural and activated zeolites were presented in the further part of this work. Natural and activated zeolites were introduced in portions (from 0.2 to 10 g) to 100 cm<sup>3</sup> of wastewater; then, the content of metal ions was determined using an inductively coupled plasma spectrometer. The experimental data showed that the application of activated zeolite enabled the removal rate of  $\text{Cr}^{3+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  close to 93%, 45%, 56% and 84%, respectively. In the case of the natural zeolite, the degree of hazardous metals removal was lower by only a few percent, but still high enough to be interesting from the practical point of view. Satisfactory effects of hazardous metal ions removal from drilling muds were achieved using 2 to 5 g of zeolite. The obtained results proved that the natural zeolite constitutes an important material for efficient removal of hazardous metal ions from drilling mud wastewater.

**Keywords:** drilling mud, zeolite, hazardous metal ions, wastewater, adsorption

### 1. Introduction

Extraction of solid minerals in Poland approximates 400 million tons per year, the majority of which include rock raw materials and fossil fuels. Extraction also yields wastes that correspond to approximately 55% of the country's deposit (Korban, 2011).

The remains from the drilling activities as well as crude oil and natural gas extraction constitute a significant share of extraction wastes. These wastes mainly include drill cuttings and spent drilling muds. The estimated amount of the produced drilling wastes in Poland amounts to about 200 thousand tons per year (Haut et al., 2007). The quantity and nuisance caused by the drilling wastes produced in the course of drilling depends on the well depth, type of the borehole and the applied drilling mud. It was observed that roughly 0.6 m<sup>3</sup> of wastes are produced from a 1 m deep borehole, approximately 60-80% of which correspond to the spent drilling muds (Onwuka et al., 2018).

Drilling fluids (muds) lubricate and cool the bits, aid in extracting the drilling cuttings to the surface, control the formation pressures, and allow good drilling performance (Gomes, 2012). Water or a mixture of natural oils, air and gas are used as the main drilling mud component (Onwukwe and Nwakaudu, 2012). Additionally, drilling muds comprise various chemical compounds, mixtures of lubricants, surfactants, solvents, etc. These compounds are classified as hazardous substances found in drilling wastes (Zhou et al., 2014). The wastes also contain total dissolved solids (TDS), chloride ions, sulphate ions, dissolved organic carbon (DOC), petroleum-derived hydrocarbons and hazardous metals, such as: arsenic, barium, cadmium, chromium, copper, mercury, nickel, lead, antimony, selenium, zinc, tin and cobalt (Ball et al., 2012). Drilling wastes are a threat to the natural environment due to their variable

composition, dependent on: the properties of the rock, type of drilling fluid, drilling technology and other factors connected with the drilling operation.

Numerous chemicals in the form of drilling fluids injected during the drilling operations are consequently disposed of in the waste pit. The hazardous metals contained in the drilling fluids and additives are of major concern because of their tendency to leach from the waste pit into the surroundings, causing environmental contamination (Moseley, 1983). The presence of hazardous metals in the drilling wastes is especially dangerous, since they are not biodegradable and tend to accumulate in organisms (Fenglian and Wang, 2011). Therefore, the concentration of hazardous metals in wastes, wastewater and soils, on which the drilling is conducted, needs to be determined. In order to reduce the hazardous metals content in drilling fluids, standard methods are employed, including: ion exchange, electro dialysis, electrocoagulation and membrane filtration (Onwuka et al., 2018; Elnenay et al., 2017; Sahl et al., 2016).

The application of natural or synthetic zeolites constitutes an alternative method for reducing the hazardous metal ions. Zeolites are crystalline, naturally-occurring hydrated silicates. Their structures comprise an infinite, three-dimensional lattice of aluminium oxide and silicon oxide tetrahedrons. Isomorphous substitution of  $\text{Si}^{4+}$  by  $\text{Al}^{3+}$  results in the negative charge of zeolites. The negative charge in the zeolites is counter-balanced with the presence of  $\text{Na}^+$ ,  $\text{Ca}^{2+}$  and  $\text{K}^+$  ions in the lattice. These cations are exchangeable with some hazardous metal ions ( $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Zn}^{2+}$ ) in solution (Bosso and Enzweiler, 2002).

Zeolites are commonly employed for the removal of hazardous metal ions and nutrients, e.g. phosphate ions from water and wastewater (Kim et al., 2013; Zhang et al., 2014; Kasprzyk et al., 2018; Kasprzyk and Gajewska, 2019). They are characterized by high porosity, sorption capacity and ion exchange capacity (Davis, 2014). The studies conducted by other authors determined the usefulness of clinoptilolite adsorbents for the removal of univalent metal salts from drilling muds (Jamrozik et al., 2011).

## 2. Materials and methods

### 2.1. Materials

The research was conducted using the spent drilling muds from the Milocin well (Podkarpackie Voivodeship, Poland). The wastes were characterized by alkaline pH 8-11. The content of hazardous metals in the considered drilling muds was shown in Table 1.

Table 1. Content of hazardous metals in drilling muds

Metal	Concentration (mg/dm <sup>3</sup> )	Permissible concentration* (mg/dm <sup>3</sup> )
Zn	15.1-18.3	2.0
Cr	3.6-4.7	0.5
Cd	0.1-0.3	0.4
Pb	0.7-1.3	0.5

\* Permissible concentration of pollution indicators for industrial wastewater discharged to water or soil – Regulation of Minister of Maritime Economy and Inland Navigation of 12<sup>th</sup> July 2019 on substances especially hazardous to the aquatic environment and the conditions to be met while introducing wastewater to waters or soil as well as during the discharge of stormwater (Journal of Laws, 2019, item 1311)

A natural zeolite sample (ZN) was obtained from Andalusia Group (Warsaw, Poland) and originally came from the Sokirnica deposit located in the Zakarpattia Region in Ukraine. The main component of the zeolite material is clinoptilolite (70-75%). Cationic exchange capacity of the zeolite identified by the amount of  $\text{Ba}^{2+}$  ions in the saturated sample and desorbed by 1 M  $\text{MgCl}_2$ , as provided by the representative of the group, was about 1.5 meq/g. Table 2 presents the elemental chemical composition of the zeolite used in the research.

Natural zeolite with grain size of 0.75-1.0 mm was washed with deionised water three or four times to remove any dust. Part of the natural zeolite was activated by transforming it into mono ionic Na-

form. First, it was regenerated to the hydrogen form using 5% HCl solution; then, it was washed with deionized water. Next, it was treated with 4% NaOH solution and finally rinsed with deionized water. The air-dried samples of natural and activated zeolites were ground to approximately 125  $\mu\text{m}$  (120 mesh) size powder. The samples were then dried in an electric oven at 150–200  $^{\circ}\text{C}$  for 2–3 h before using for the adsorption purpose.

Table 2. The elemental chemical composition of the natural zeolite

Component	Value (wt. %)
SiO <sub>2</sub>	67.7
Al <sub>2</sub> O <sub>3</sub>	12.6
Fe <sub>2</sub> O <sub>3</sub>	2.00
Na <sub>2</sub> O	0.35
K <sub>2</sub> O	2.80
CaO	2.60
MgO	1.00
SO <sub>4</sub> <sup>2-</sup>	0.43

## 2.2. Sorption isotherms

The isotherms of hazardous metal sorption on zeolites were determined with the static method of separate weighed amounts. The samples of zeolite (1 g each) were poured with 45 cm<sup>3</sup> of deionized water and 0.01 M working solution of hazardous metal in the amounts ranging from 0.1 to 1 cm<sup>3</sup> were introduced afterwards. The working solutions of hazardous metals were prepared from corresponding salts in demineralized water, i.e. CdCl<sub>2</sub>·3H<sub>2</sub>O, ZnCl<sub>2</sub>, Cr(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, and Pb(NO<sub>3</sub>)<sub>2</sub>. Then, pH was measured and adjusted to the value of 6 using 0.1 M solutions of HCl or NaOH. After topping up with water to 50 cm<sup>3</sup>, the bottles were shaken for 24 h (to ensure steady-state condition). Then, the equilibrium concentrations of hazardous metals in the solution were determined with the ICP method using JY 238 Ultrace sequential ICP-OES spectrometer (ISA Jobin Yvon, France).

The amount of hazardous metal adsorbed onto zeolite was calculated from the difference between the introduced amount and the amount remaining in the state of equilibrium. Similar investigations were conducted for all studied hazardous metals, i.e. cadmium, chromium, lead and zinc.

The obtained data was fitted to Langmuir and Freundlich isotherms. The Langmuir equation has the following form:

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

where:  $C_e$  – the equilibrium concentration of metal ions in solution (mg/dm<sup>3</sup>);  $q_e$  – the amount of the metal ions sorbed per unit mass of the sorbent (mg/g);  $q_m$  – the maximum amount of metal ions covering the surface of the sorbent (monolayer capacity) (mg/g);  $K_L$  – the Langmuir isotherm constant, characteristics of particular system (dm<sup>3</sup>/mg).

The essential characteristics of the Langmuir isotherm can be expressed by a separation factor or equilibrium constant  $K_R$ , which is defined as:

$$K_R = \frac{1}{1 + K_L C_0} \quad (2)$$

where:  $K_R$  – dimensionless separation factor;  $C_0$  – initial concentration of hazardous metal ions in the solution (mg/dm<sup>3</sup>);  $K_L$  – the Langmuir isotherm constant (dm<sup>3</sup>/mg).

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  $K_R = 1$  the type of isotherm is linear (Deepthi Rani and Sasidar, 2012). The Freundlich equation is an empirical relationship and has the following form:

$$q_e = K_F (C_e)^{\frac{1}{n}} \quad (3)$$

where:  $K_F$  is correlated with the quantity of the 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 (Ho and Wang, 2004).

### 2.3. Influence of pH on the sorption of hazardous metals ions on a zeolite

A row of 50 cm<sup>3</sup> plastic bottles containing 0.5 g of natural zeolite each was prepared; then, the samples were poured with distilled water and variable amounts of 0.1 M HCl or NaOH solutions were added. Following a thorough mixing, 1 cm<sup>3</sup> of the solution containing one of the considered hazardous metals ions (Cd, Pb, Cr, and Zn) with the concentration of 0.01 M was added to each bottle. Afterwards, the content of bottles was topped up to 50 cm<sup>3</sup> with demineralized water and the samples prepared in such way were placed on a shaker. After 2 h, the pH of all samples was measured and the concentration of metals was determined with the ICP method.

### 2.4. Removal of hazardous metals ions from drilling wastewater

Natural and activated zeolites in the amounts of 0.2; 0.5; 1; 2; 5; and 10 g were added to 100 cm<sup>3</sup> of spent drilling muds. The samples were shaken for 24 h on a horizontal shaker. The experiment was conducted in three parallel repetitions. Then, 10 cm<sup>3</sup> of drilling wastes were collected and poured with distilled water, in line with the PN-EN 12457-2:2006 standard. The samples of water extract were subjected to mineralization in nitric(V) acid (3 cm<sup>3</sup>). The mineralization process lasted for 45 min at a temperature of 180 °C and the pressure of 18 bars. The metal ions concentrations were determined with the ICP method. The adsorption percent (%R) was calculated using the following formula:

$$\%R = \frac{c_i - c_f}{c_f} 100\% \quad (4)$$

where: %R – adsorption percent;  $c_i$  and  $c_f$  – concentration of the investigated metal ions before and after extraction.

## 3. Results and discussion

### 3.1. Adsorption isotherms

The adsorption isotherms are the basic relations enabling description of the properties of sorption materials and evaluate their usefulness, which is indispensable while designing adsorption systems. The determined experimental amounts of sorbed hazardous metal ions ( $q_e$ ), depending on their equilibrium concentration in the solution ( $C_e$ ), are presented in Figure 1. The sorption process was described with Freundlich and Langmuir equations. The constants in mathematical models were determined with the least squares method using the Statistica software package; then, the errors related to the constants were indicated. The values of parameters for Langmuir and Freundlich isotherms used in this study are presented in Table 3.

Table 3. The values of parameters for Langmuir and Freundlich isotherms

Isotherm type	Coefficient	Cd <sup>2+</sup>	Cr <sup>3+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>
Freundlich	1/n	0.453	0.488	0.379	0.531
	K <sub>F</sub> (dm <sup>3</sup> /g)	0.919	0.584	1.025	1.098
	R	0.976	0.940	0.956	0.984
Langmuir	q <sub>m</sub> (mg/g)	7.070	1.430	4.420	3.970
	K <sub>L</sub> (dm <sup>3</sup> /mg)	0.069	0.216	0.109	0.117
	K <sub>R</sub>	0.879	0.523	0.925	0.863
	R	0.977	0.953	0.956	0.983

While comparing the hazardous metal ions sorption isotherms it was observed that they are linear in relation to cadmium, lead and zinc ions. In the case of chromium ions, the amount adsorbed in the solution decreases exponentially as the concentration of metal ion increased.

For the considered concentrations of hazardous metal ions in the solution, the curves representing adsorption on natural zeolite are sufficiently well described by Freundlich and Langmuir isotherm

formulae. The obtained values of correlation coefficients exceeded 0.94. The usage of two isotherm models for ion adsorption suggests that monolayer and heterogeneous surfaces are formed during the adsorption process (Bus and Karczmarczyk, 2014).

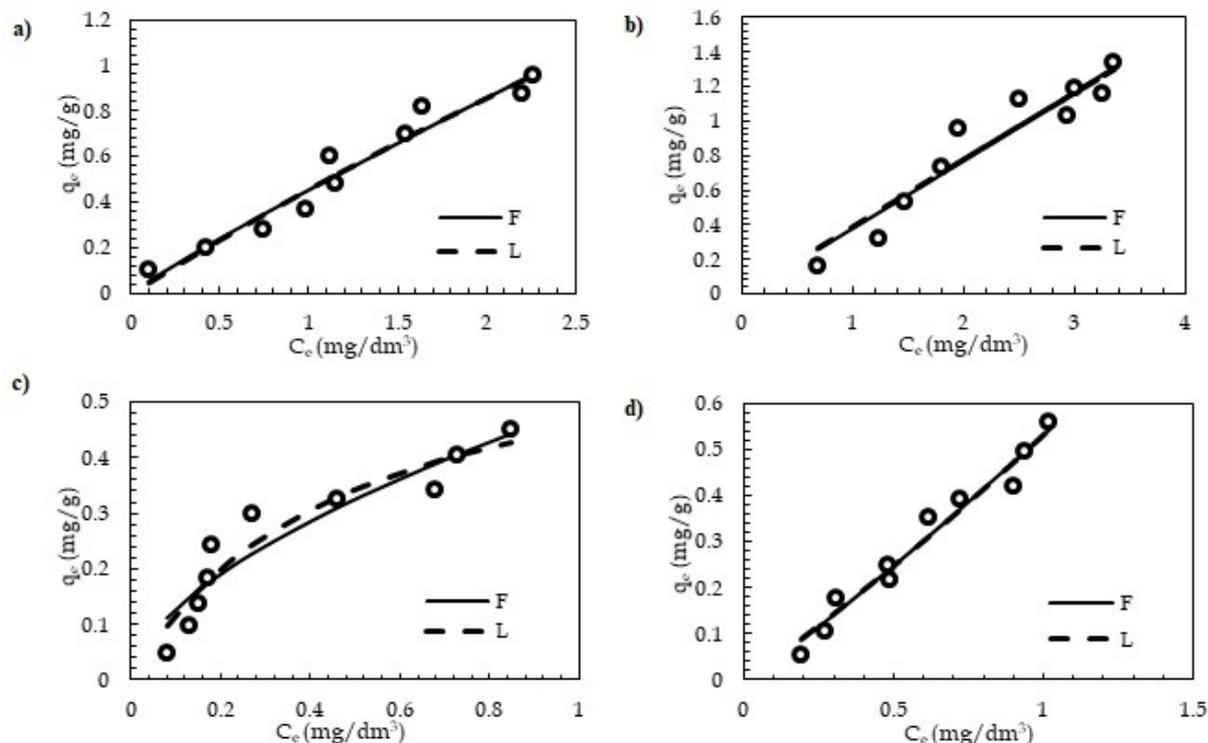


Fig. 1. Adsorption of metal ions onto natural zeolite fitted to Langmuir (L) and Freundlich (F) isotherm models: a)  $\text{Cd}^{2+}$ , b)  $\text{Cr}^{3+}$ , c)  $\text{Pb}^{2+}$  and d)  $\text{Zn}^{2+}$

Therefore, it can be stated that the reduction degree of the considered hazardous metals in solutions, with the use of zeolites, results both from the adsorption in micropores, as well as monolayer adsorption on the adsorbent surface (Limousin et al., 2007). With respect to the Langmuir isotherm, the sorption process is carried out at homogeneous sites of sorbent (Maurya and Mittal, 2006). Similar results have been reported by various researchers who applied the Langmuir model to explain the hazardous metal ions removal by various types of zeolites (Taffarel and Rubio, 2010). Good match of the considered sorption models with the experimental data confirms the usefulness of natural zeolite in the reduction of hazardous metal ions from solutions. The coefficient  $q_m$ , corresponding to the sorption capacity, has comparably high values for the considered hazardous metals, except for chromium, for which the zeolite indicates lower sorption capacity. The sorption capacity of natural zeolite for the studied hazardous metals was in the following order:  $\text{Cd}^{2+} > \text{Pb}^{2+} > \text{Zn}^{2+} > \text{Cr}^{3+}$ . The obtained and presented results of the sorption experiment justify the application of the investigated zeolite for the disposal of spent drilling muds.

### 3.2. Effect of pH

The efficiency of hazardous metal ions removal using natural zeolite, depending on the pH of the drilling fluid, was presented in Figure 2. It was observed that efficient removal of zinc ions (>90%) occurred at pH 4÷8, chromium ions - at pH 5÷7, while cadmium ions - at pH 7÷9. Lead ions are efficiently removed regardless of the pH value. High degree of lead ions reduction was connected with their largest size among the investigated hazardous metal ions and the fact that they are characterized by the strongest physical adsorption in zeolite pores. At a given pH of the drilling fluid solution, the selectivity of zeolite in relation to a given metal is dependent on its dominant form and the created complexes (Yasin et al., 2017).

The results indicate a strong adsorption of  $\text{Cd}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  at the pH range of 5 to 7. The greatest ion reduction degree was observed for pH 7. Therefore, the neutral pH of the drilling fluid is conducive to the adsorption process. At lower pH (<4.0) for  $\text{Cr}^{3+}$ ,  $\text{Zn}^{2+}$ , the metal and hydrogen ions might compete for bonds on the adsorbent surface (Zheng et al., 2000).

In the study on the removal of metals from spent drilling muds using kaolinite and synthetic zeolites from fly ash, Yasin (2017) indicated the optimal pH value for  $\text{Cr}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Fe}^{2+}$  removal, ranging from 4.5 to 6.

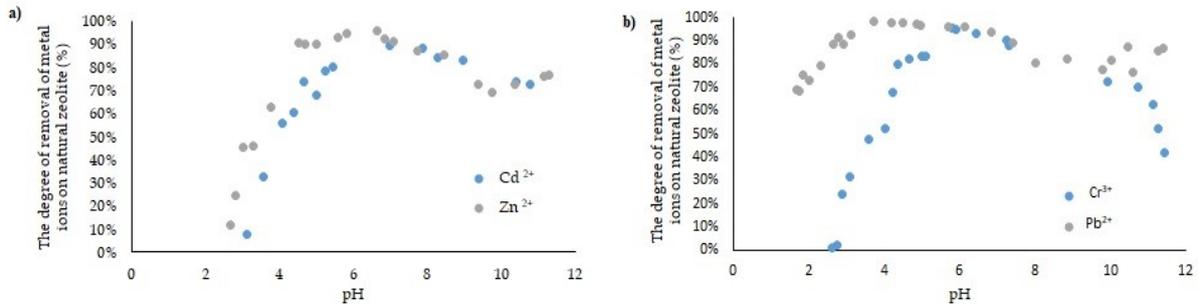


Fig. 2. Influence of pH on the degree of metal ions removal by natural zeolite: a) cadmium and zinc, b) chromium and lead

### 3.3. Effect of activated zeolite dosage on adsorption capacity and adsorption rate in drilling mud

The adsorbent dose is the main parameter governing the efficiency of metal ions removal through adsorption. Increasing the adsorbent dose ensures better contact surface and greater adsorption capacity (Kocaoba, 2007). The influence of zeolite dose on the removal of  $\text{Cd}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Zn}^{2+}$  from spent drilling muds was presented in Figs. 3 and 4.

Addition of natural zeolite enables to obtain the lowest concentrations of  $\text{Cr}^{3+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  ions in the doses amounting to 2 and 5 g. The application of a larger dose (10 g), both in the case of the activated and natural zeolite, did not result in a further decrease in the concentration of investigated metal ions. For  $\text{Zn}^{2+}$ , the lowest concentration was obtained using 5 g and 10 g of both zeolites. Both the activated and natural zeolite exhibited the highest efficiency of removing the considered hazardous metals at the dose of 2 and 5 g.

The calculated values pertaining to the degree of hazardous metal ions reduction in drilling fluids are presented in Figure 5. It was noted that the degree of hazardous metal reduction increased along with the dose of zeolites. The greatest reduction was obtained for chromium and cadmium ions. Using the natural zeolite, it was possible to reduce the chromium, cadmium, zinc and lead ions by 91%, 80%, 54% and 41%, respectively. In turn, the application of the activated zeolite yielded only marginally better results, i.e.  $\text{Cr}^{3+}$  – 93%,  $\text{Cd}^{2+}$  – 84%,  $\text{Zn}^{2+}$  – 56%, and  $\text{Pb}^{2+}$  – 45%.

In the study on spent drilling muds, Yasin et al. (2017) obtained slightly higher reduction of the considered metals using the synthetic zeolite, reaching 99%, 97%, 98% and 80% for  $\text{Cr}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Fe}^{2+}$ , respectively; in turn, lower metal ions concentration reduction values were obtained for conite, reaching 72.8%, 78.6%, 77.9% and 34% for  $\text{Cr}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Fe}^{2+}$ , respectively.

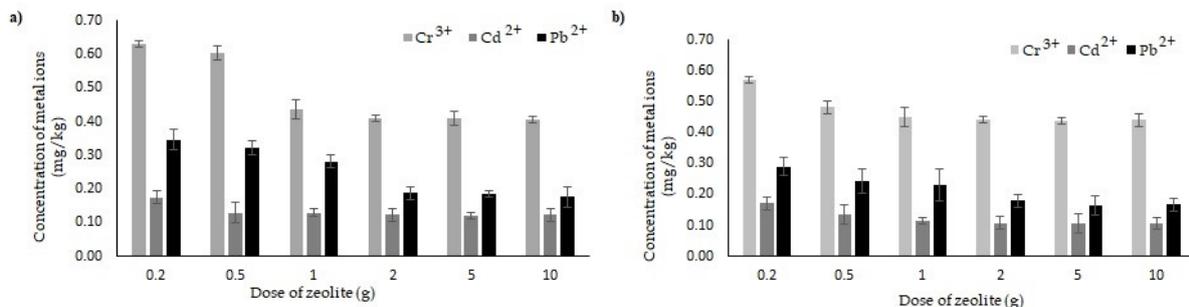


Fig. 3. Effect of sorbent dose on reduction of  $\text{Cr}^{3+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  concentration using: a) natural and b) activated zeolites

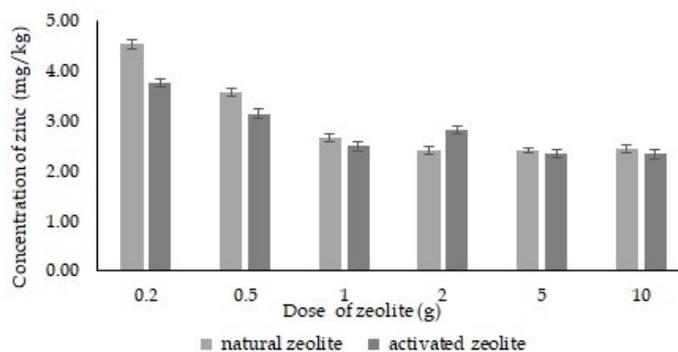


Fig. 4. Effect of sorbent dose on reduction of Zn concentration using natural and activated zeolites

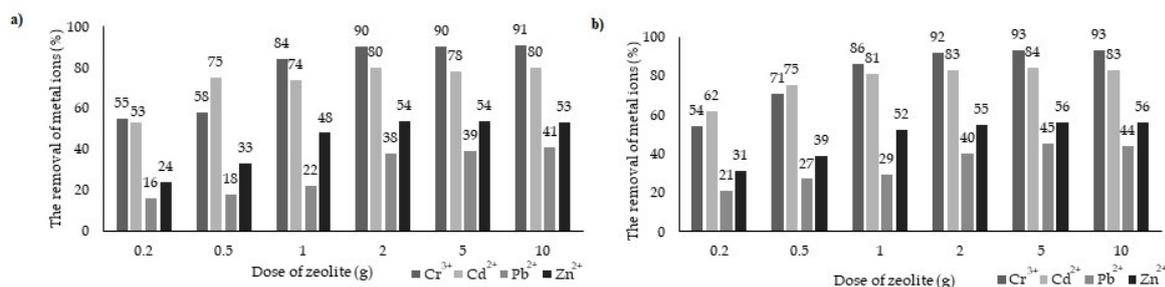


Fig. 5. The removal of metal ions from mud samples using: a) natural and b) activated zeolites

#### 4. Conclusions

The following conclusions were drawn from the results obtained in the research:

- the studies on the adsorption of chromium, zinc, cadmium and lead on natural zeolite indicated very good properties for the reduction of hazardous metal ions amount in highly polluted solutions;
- in the case of removal of chromium, zinc, and cadmium ions, the drilling mud solution should be characterized by the pH as close to neutral, while the lead ions can be removed in a wide range of pH;
- the purposefulness of applying zeolites for the removal of hazardous metals in spent drilling muds was confirmed. The best results were obtained while reducing the chromium and cadmium ions, the content of which was reduced by 93% and 84%, respectively;
- good results were obtained for reducing the hazardous metal ions from spent drilling muds using 2-5 g of zeolite per 100 cm<sup>3</sup> of drilling mud;
- in comparison to the natural zeolite, the application of activated zeolite did not result in a marked improvement in the efficiency of hazardous metal ions removal.

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