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ADSORPTION OF Pb^{2+} AND Zn^{2+} IONS FROM AQUEOUS SOLUTIONS WITH NATURAL ZEOLITE

Vira Sabadash[1] ✉, Anna Nowik-Zając[2], Jaroslaw Gumnitsky[1]

[1] Lviv Polytechnic National University,
12, S. Bandery str., Lviv, 79013, Ukraine
[2] Jan Dlugosz University in Czestochowa,
4/8, J. Washington str., 42200, Częstochowa,
vira.v.sabadash@lpnu.ua

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Abstract. Pollution of the aquatic environment with heavy metals, particularly lead (Pb^{2+}) and zinc (Zn^{2+}) ions, is one of our most pressing environmental problems. Even insignificant concentrations of Pb^{2+} and Zn^{2+} ions in the water pose a serious threat to human health, biodiversity, and the functioning of aquatic ecosystems. The work aims to assess the effectiveness of zeolite as a low-cost natural sorbent for purifying the aquatic environment from toxic metals. The experimental part was carried out by a series of laboratory studies under static conditions at a temperature of 20 °C, with a variation of the initial concentrations of metal solutions within 1–30 mg/dm³. The sorbent interacted with the solutions for 48 hours, after which the residual concentration of ions in the filtrate was determined by ionometry and photometry. The obtained adsorption equilibrium data are consistent with the classical Langmuir and Freundlich isotherms. In particular, for zinc ions, it was found that the equilibrium dependence is well approximated by the Langmuir equation with a high coefficient of determination ($R^2 > 0.97$). The Freundlich isotherm also showed satisfactory correspondence to the experimental data, which indicates the heterogeneity of the active centres of the sorbent. A comparative analysis of the adsorption capacity showed that natural zeolite has a higher efficiency in removing Pb^{2+} ions than Zn^{2+}, which is explained by the physicochemical properties of the ions (in particular, the radius and hydration energy). The results indicate the feasibility of using zeolite as a sorbent for preliminary water purification from heavy metals.

Keywords: wastewater, heavy metals, adsorption isotherm, zeolite, ecological security.

1. Introduction

Pollution of water resources with heavy metals, particularly lead (Pb^{2+}) and zinc (Zn^{2+}) ions, is one of our most acute environmental problems. These metals are toxic even at low concentrations and can accumulate in living organisms, causing severe ecosystem disturbances and threatening human health. In this regard, the search for effective, affordable and environmentally safe methods for removing heavy metal ions from polluted waters is relevant. Among such methods, adsorption using natural materials, particularly zeolites, which have a high cation exchange capacity, a developed porous structure and significant availability, attracts considerable attention. However, the effectiveness of natural zeolites in removing specific ions, such as Pb^{2+} and Zn^{2+}, depends on several factors – the type of zeolite, process conditions, ion concentration and the competitive influence of other components. This necessitates a more detailed study of the adsorption capacity of natural zeolite for lead and zinc ions to optimise the water purification parameters.

Under modern industrial development, the technogenic load on the environment is increasing, which causes an increase in the concentration of heavy metals in water bodies. Lead (Pb^{2+}) and zinc

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(Zn^{2+}) ions are among the most common pollutants entering water bodies with industrial and mining wastewater. These elements are highly toxic, capable of bioaccumulation, and pose a serious threat to aquatic ecosystems and human health. Traditional water purification methods, particularly chemical precipitation or membrane technologies, are often energy-intensive and expensive or create secondary waste.

In modern research, considerable attention has been focused on the adsorption of heavy metal ions, in particular Pb^{2+} and Zn^{2+}, from aqueous solutions by various natural and modified sorbents (Astuti et al., 2017) and investigated the competitive adsorption of Pb^{2+} and Zn^{2+} on modified fly ash, highlighting the effectiveness of such material in water purification. Similarly, Chafik et al. (Chafik et al., 2024) demonstrated that the properties of biochar obtained from different raw materials significantly affect its ability to sorb Pb^{2+} and Zn^{2+} ions. By using modelling, researchers have shown the interaction of metal ions with the surfaces of microstructures (Chavez-Martinez et al., 2021), and (Fatma et al., 2024) found that activated green tamarind pulp is an effective biosorbent for the removal of several ions, including Pb^{2+}, Cu^{2+}, Zn^{2+} and Ni^{2+}. In a study (Ferri et al., 2024), natural zeolite also showed good adsorption properties for removing organic pollutants, confirming its multifunctionality. The study Yusubov & Namazova (Yusubov & Namazova, 2024) outlines the features of the sorption of Pb^{2+}, Cd^{2+} and Zn^{2+} ions from industrial wastewater, emphasising the importance of modifying natural materials to improve treatment efficiency. The study (Ghasemi, 2023) also notes the potential of photocatalytic membranes for removing heavy metals from water, complementing classical adsorption methods. Other authors, in particular (Gumnitsky et al., 2022) and (Sabadash & Omelianova, 2021), investigated the dynamics and predicion of environmental ion migration. The work (Lawal et al., 2024) demonstrates competitive adsorption of Pb^{2+}, Z^{2+} and Fe^{2+} on modified clay, while (Lazar et al., 2023) describe the use of ion-imprinted polymers for selective sorption. An innovative approach to creating new adsorbents is demonstrated by (Sadeghi & Zarshenas, 2022) using zeolite-based nanocomposites. Investigation of adsorption (Sydorchuk et al., 2014) considered the processes of serial-parallel adsorption of phosphates, which is also important in studying the interaction mechanisms with natural sorbents. The authors Wang et al. (Wang et al., 2024) synthesised MER-zeolite with a high ability to remove Pb^{2+} and Cd^{2+} and (Youssif et al., 2024) provided a systematic review of the use of nanomaterials for heavy metal adsorption. Finally, a study (Zhang et al., 2024) showed that modified coal gangue adsorbs Pb^{2+} and Zn^{2+} well, especially after ball milling. In this context, due to their sorption properties, ion exchange capacity and availability, natural zeolites are considered promising materials for water purification from heavy metals. However, the effectiveness of using natural zeolite for the removal of Pb^{2+} and Zn^{2+} from aqueous solutions depends on many factors that require careful study. Therefore, studying the adsorption mechanisms of these ions using natural zeolite is of great importance both in scientific and practical aspects, especially for developing cheap and environmentally friendly water purification technologies.

Research objective

The study aims to establish the effectiveness of natural zeolite as an adsorbent for removing lead (Pb^{2+}) and zinc (Zn^{2+}) ions from aqueous adsorption solutions and optimising purification conditions.

2. Materials and methods

Methodology for studying the adsorption of Pb (II) and Zn (II) ions by natural zeolite

Preparation of solutions and conduct of a sorption experiment

A series of model solutions of lead (Pb^{2+}) and zinc (Zn^{2+}) ions with initial concentrations ranging from 1 to 30 mg/dm³ were prepared to construct adsorption isotherms. For each experimental sample, 50 ml of the solution of the corresponding concentration was placed in a separate 100 ml chemical flask, and 2.00 ± 0.01 g of previously prepared natural zeolite was added.

The flasks were tightly closed with lids and placed in a thermostat at 20 ± 1 °C. For 48 hours, the samples were subjected to periodic mixing to ensure an equilibrium distribution of ions between the solid and liquid phases. After the contact of the solid and liquid phases was completed, the samples were filtered through filter paper of the "blue ribbon" type.

Ionometric determination of Pb (II) and Zn (II) concentrations in solutions

The filtrate was analysed by direct tonometry using combined ion-selective electrodes sensitive to Pb^{2+} and Zn^{2+}. To ensure the accuracy of the measurements, a background electrolyte (e. g., KNO_3 or $(NH_4)_2SO_4$ solution) was added to each sample to stabilise the medium's ionic strength. The measurements were performed using a digital tonometer previously calibrated with standard buffer solutions with known concentrations of Pb^{2+} and Zn^{2+}.

Additional control methods

After the adsorption process, the solid phase (zeolite) was dried to constant mass at 105 °C. The content of adsorbed Zn^{2+} and Pb^{2+} ions in the samples was determined using X-ray fluorescence (XRF) analysis. These results allowed us to clarify the number of absorbed ions, which correlated with the results of the ionometric analysis.

3. Results and discussion

During the study, a series of experiments were conducted to study the adsorption capacity of natural zeolite for Pb^{2+} and Zn^{2+} ions in aqueous solutions. The influence of key parameters, such as the initial concentration of metal ions, pH of the medium, contact time between the adsorbent and the solution, and the dose of the sorbent, was evaluated. The results allowed us to identify the regularities of the adsorption processes, establish optimal conditions for maximum ion extraction from the solution, and compare the sorption efficiency for each studied metal. Fig. 1 shows the adsorption isotherm of Pb^{2+} ions from aqueous solutions by natural zeolite.

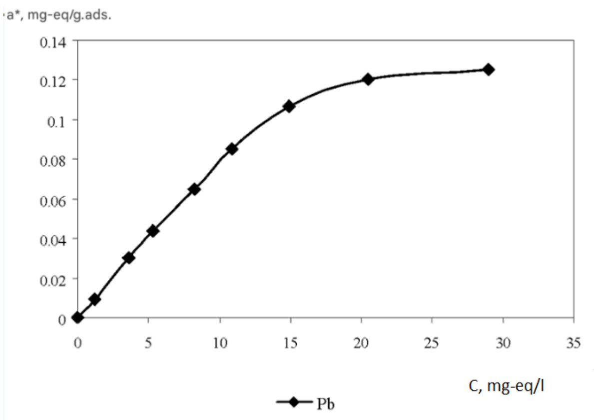

Fig. 1. Pb^{2+} adsorption isotherm on natural zeolite

Fig. 1 shows the dependence of the adsorption value (a^*, mg-eq/g of adsorbent) on the equilibrium concentration of Pb^{2+} ions in the solution (C, mg-eq/dm³). The dependence has a characteristic *S-shaped shape*, which indicates the initial gradual saturation of the adsorbent's active centres and then a decrease in the adsorption rate with increasing Pb^{2+} concentration.

In the initial concentration range (up to ~15 mg-eq/dm³), *an almost linear increase* in adsorption is observed, which indicates a high availability of free active centres on the zeolite surface. With a further increase in concentration (over 20 mg-eq/dm³), the curve gradually reaches a plateau, which indicates the achievement of an approximate saturation state – the number of available centres decreases, and the process enters a limited adsorption regime. The linearised isotherm is presented in Fig. 2.

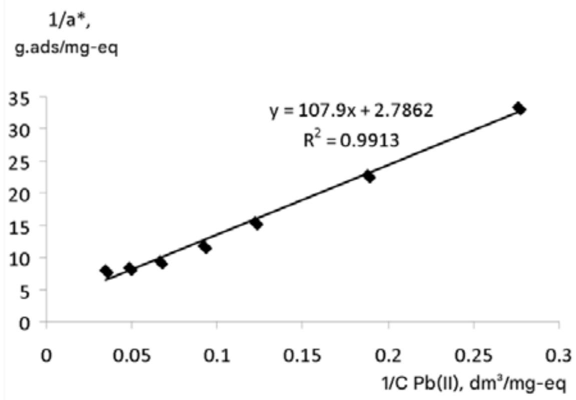

Fig. 2. Linearised Langmuir adsorption isotherm for Pb^{2+} on natural zeolite

The equilibrium isotherm equation according to the Langmuir equation with a coefficient of determination of 0.9913 has the form:

$$a^* = 0.39 \cdot \frac{0.02C}{1+0.02C}. \quad (1)$$

This form of the isotherm corresponds to Langmuir-type isotherms (Fig. 2) or Freundlich (Fig. 3), which are characteristic of monomolecular adsorption on a homogeneous or weakly heterogeneous surface. The maximum value of Pb^{2+} adsorption reaches about 0.13 mg-eq/g of adsorbent. The isotherm indicates a high affinity of the zeolite for Pb^{2+} at the initial stages of contact. There is a tendency to saturation, which confirms the limited number of adsorption-active centres.

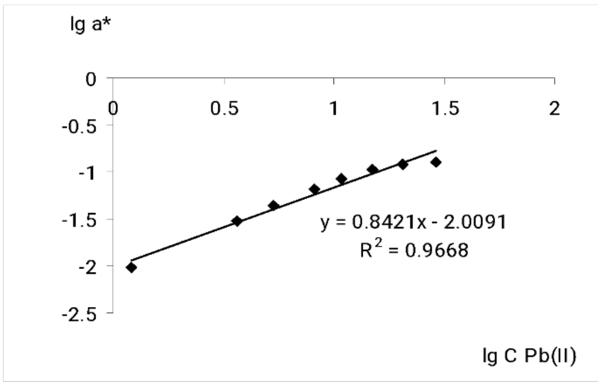

Fig. 3. Linearised Freundlich adsorption isotherm for Pb^{2+} on natural zeolite

Fig. 3 presents a linearisation of the adsorption equilibrium data according to the Freundlich isotherm. As can be seen from Fig. 3, the experimental results are approximated by a linear relationship with a coefficient of determination of 0.9668, which indicates the adequacy of the theoretical model.

The equilibrium equation will look like this:

$$a^* = 0.01 \cdot C^{0.8421}, \quad (2)$$

the Langmuir equation is more reliable.

Adsorption of Zn (II) i ons from aqueous solutions by natural zeolite

The adsorption isotherm for Zn (II) ions, constructed based on the results of experimental studies, is described by an equation of the form:

$$a^* = 0.2 \cdot \frac{0.026C}{1+0.026C}, \quad (3)$$

where a is the adsorption value, mg-eq/g of zeolite; C is the equilibrium Zn (II) concentration in solution, mg-eq/dm³.

Equation (3) corresponds to the form of the Langmuir isotherm, which indicates the monolayer adsorption of zinc on the zeolite surface with a limited number of active centres. The obtained data indicate the saturation of adsorption centres with increasing Zn (II) c oncentration in the solution, after which the adsorption value reaches a limit value close to 0.39 mg-eq/g of zeolite (Fig. 4). The constant 0.02 in the equation characterises the affinity (affinity) of the adsorbent to Zn (II) i ons. Compared with Pb (II) i ons, this value is lower, which indicates a lower affinity of natural zeolite to zinc. This is confirmed both by experimental observations and by the physicochemical properties of the ions: the smaller ionic radius of Zn (II) and lower electronegativity reduce its ability to interact with the active centres of the adsorbent.

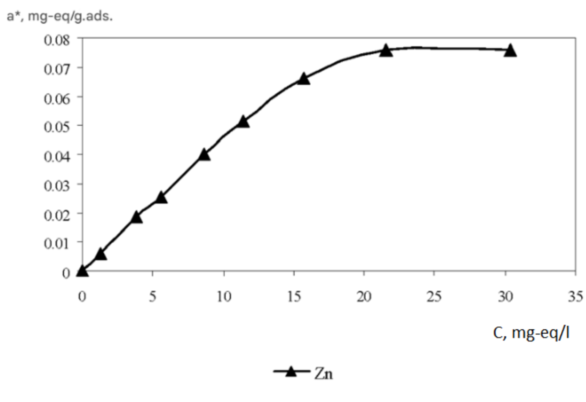

Fig. 4. Zn^{2+} adsorption isotherm on natural zeolite

Therefore, according to the results obtained, natural zeolite effectively adsorbs Zn (II) ions from the aqueous environment, although to a lesser extent than Pb (II), which must be considered when using it in wastewater treatment systems for heavy metals.

The linearised adsorption isotherm of Zn^{2+} on natural zeolite is presented in Fig. 5.

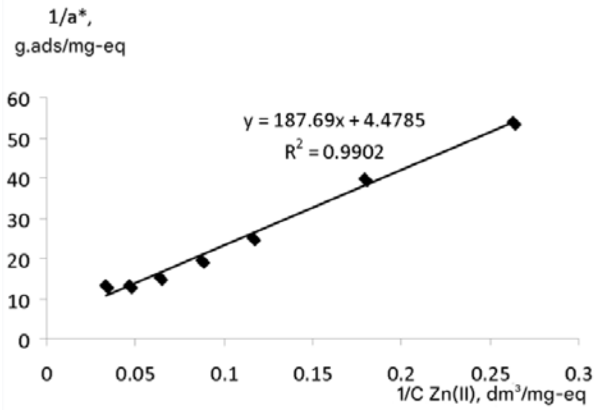

Fig. 5. Linearised Langmuir adsorption isotherm for Zn^{2+} on natural zeolite

The linearised form of the Freundlich isotherm was applied to model the equilibrium adsorption of Zn (II) ions by natural zeolite, and the results are shown in Fig. 6.

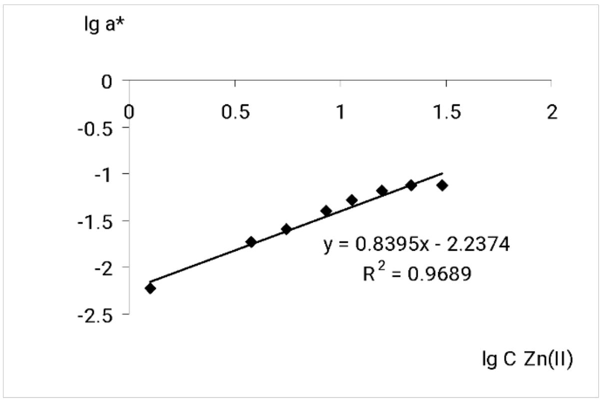

Fig. 6. Linearised Freundlich adsorption isotherm for Zn^{2+} on natural zeolite

The obtained linear relationship between the logarithm of the equilibrium concentration and the logarithmic type adsorption value has a high coefficient of determination $R^2 = 0.9668$, which indicates a good fit of the experimental data to the Freundlich model.

The isotherm equation has the form:

$$a^* = 0.01 \cdot C^{0.8395}, \quad (4)$$

where a^* is the equilibrium adsorption value, g ads/mg-eq; C is the equilibrium concentration of Zn(II), mg-eq/dm³.

The coefficient $n = 0.8395$ is less than 1, which indicates a decrease in adsorption efficiency with an increasing metal concentration in the solution − a characteristic sign of the uneven distribution of energy of adsorption centres on the zeolite surface.

However, a comparison of the approximation results by Freundlich and Langmuir isotherms indicates the latter model's superiority. The Langmuir isotherm's coefficient of determination is $R^2 = 0.9902$, which indicates a higher accuracy in describing the experimental data and confirms the assumption of the monomolecular nature of adsorption on the homogeneous surface of natural zeolite.

Thus, although the Freundlich model describes the sorption process quite well, the Langmuir model is more suitable for characterising the interaction of Zn (II) ions with natural zeolite under the studied conditions.

Comparison of lead and zinc adsorption isotherms indicates that lead has a higher affinity for zeolite than zinc. In particular, the configuration of the obtained Pb^{2+} adsorption isotherm indicates that after saturation of the zeolite surface with a monomolecular layer of metal ions, the adsorption process does not stop. Instead, further absorption occurs, leading to the formation of polymolecular adsorption layers. This behaviour indicates a complex interaction mechanism of lead ions with the surface of natural zeolite, which combines physical adsorption, ion exchange and, probably, weak chemical bonds. Analysing the obtained data, it can be stated that despite the dominant cation-exchange properties of zeolite, Pb^{2+} ions exhibit a higher affinity for the adsorbent than Zn^{2+}. This may be due to the greater polarisation of lead, its greater electronegativity (Pb^{2+} – 2.33; Zn^{2+} – 1.65 on the Pauling scale), as well as a larger ionic radius (147 pm versus 131 pm, respectively), which contributes to better interaction with the active centres of zeolite. In addition to the adsorption of heavy metal ions, ion exchange occurs in parallel between solution cations (in particular, K^+) and exchange ions in the zeolite structure. Qualitative reactions confirmed the presence of Na^+, K^+, Ca^{2+} and Mg^{2+} cations in the solution after contact with the adsorbent, consistent with literature sources and confirming the mechanism of ion exchange as one of the components of the sorption process. The experimental results indicate a high sorption capacity of natural zeolite for Pb^{2+} and Zn^{2+} ions, emphasising the prospects of its use for purifying aquatic environments from heavy metal pollution. The order of efficiency of removal of heavy metal ions in the study corresponds to Pb (II) > Zn (II), which is explained by a complex of factors − in particular, ionic radius, charge and electronegativity. In multicomponent systems, the ionic radius and the nature of the interaction with the active centres of the adsorbent play a decisive role in the sorption processes.

4. Conclusions

Experimental results confirm the effectiveness of natural zeolite as an affordable and environmentally safe sorbent for removing lead (Pb^{2+}) and zinc (Zn^{2+}) ions from aqueous solutions. The sorption process exhibits good dynamics at a temperature of 20 °C and a contact period of 48 hours, which makes it suitable for use in natural environments and low-cost technologies. Analysis of adsorption isotherms showed that the Langmuir model most accurately describes the system's equilibrium state, which indicates the formation of a monomolecular layer of adsorbed ions on the zeolite surface. Zeolite demonstrates a higher affinity for Pb^{2+} ions than Zn^{2+}, which is explained by the larger ionic radius of lead and lower hydration energy. The sequence of sorption efficiency of heavy metals is given in the order: $Pb^{2+} > Zn^{2+}$. These results are consistent with the literature data on the nature of ion exchange on the surface of aluminosilicates. An important accompanying process is the ion exchange between cations in the solution (Na^+, K^+, Ca^{2+}, Mg^{2+}) and cations in the zeolite structure, affecting the overall purification efficiency. Qualitative reactions and X-ray fluorescence analysis confirmed it. The results obtained have significant practical potential for purifying wastewater and natural waters from heavy metal ions, especially in regions with increased technogenic load. Natural zeolite can be recommended as a low-cost, stable and renewable material for creating filtration systems and sorption barriers.

In further studies, it is advisable to study the process's kinetic characteristics and the influence of pH and conduct adsorption modelling under dynamic conditions, which will allow scaling of the technology for industrial application.

References

Astuti, W., Martiani, W., & Khair N., A. I. (2017). Competitive adsorption of Pb^{2+} and Zn^{2+} ions from aqueous solutions by modified coal fly ash In *Engineering International Conference (EIC) 2016: Proceedings of the 5th International Conference on Education, Concept, and Application of Green Technology*, 1818, 020007. DOI: https://doi.org/10.1063/1.4976871

Chafik, Y., Hassan, S. H., Lebrun, M., S ena-Velez, M., Cagnon, B., Carpin, S., Boukroute, A., Bourgerie, S., & Morabito, D. (2024). Biochar characteristics and Pb^{2+}/Zn^{2+} sorption capacities: the role of feedstock variation. *International Journal of E nvironmental Science and Technology*. 21, 9829–9842. DOI: https://doi.org/10.1007/s13762-024-05646-0

Chavez-Martinez, E. H., Cedillo-Cruz, E., & Dominguez, H. (2021). Adsorption of metallic ions from aqueous solution on surfactant aggregates: a molecular dynamics study. *Condensed Matter Physics*, *24* (2), 23601. https://doi.org/10.5488/cmp.24.23601

Fatma, U. K., Nizami, G., Ahamad, S., Saquib, M., & Hussain, M. K. (2024). Activated Green Tamarind Pulp (AGTP) as an efficient adsorbent for removal of Pb^{2+}, Cu^{2+}, Zn^{2+} & Ni^{2+} from contaminated water. *Journal of Water Process Engineering*, *59*, 105048. DOI: https://doi.org/10.1016/j.jwpe.2024.105048

Ferri, B. B., Wernke, G., Resende, J. F., Ribeiro, A. C., Cusioli, L. F., Bergamasco, R., & Vieira, M. F . (2024). Natural zeolite as adsorbent for metformin removal from aqueous solutions: adsorption and regeneration properties. *Desalination and Water Treatment*, *320*, 100602. DOI: https://doi.org/10.1016/j.dwt.2024.100602

Yusubov, F. V., & Na mazova, S. R. (2024). Features of adsorption of heavy metal ions Pb^{2+}, Cd^{2+} and Zn^{2+} from wastewater in environmental protection. *PAHTEI-Proceedings of Azerbaijan High Technical Educational Institutions*, *148* (02-02), 430–437. DOI: https://doi.org/10.36962/pahtei14802-022024-430

Ghasemi, S. (2023). Heavy Metal Removal from Wastewater via Photocatalytic Membrane. In *Membrane Technologies for Heavy Metal Removal from Water* CRC Press. DOI: https://doi.org/10.1201/9781003326281-13

Gumnitsky, J., Sabadash, V., Matsuska, O., Lyuta, O., Hyvlud, A., & Venger, L. (2022). Dynamics of Adsorption of Copper Ions in Fixed Bed Column and Mathematical Interpretation of the First Stage of the Process. *Chemistry & Chemical Technology*, *16*(2), 267–273. DOI: https://doi.org/10.23939/chcht16.02.267

Lawal, J. A., Olaremu, A. G., Odeyemi, O. T., Omei za, F. S., & Sann, I. (2024). Competitive adsorption of Fe^{2+}, Pb^{2+}, and Zn^{2+} ions from multi-metal ion solution on ammonium oxalate-modified kaolinite clay. *Journal of Chemical Society of Nigeria*, *49*(3). DOI: https://doi.org/10.46602/jcsn.v49i3.991

Lazar, M. M., Ghiorghita, C.-A., Dragan, E. S., Humelnicu, D., & Dinu, M. V. (2023). Ion-Imprinted Polymeric Materials for Selective Adsorption of Heavy Metal Ions from Aqueous Solution. *Molecules*, *28*(6), 2798. DOI: https://doi.org/10.3390/molecules28062798

Sabadash, V., & Omelianova, S. (2021). Mathematical prediction of the scale of migration of heavy metals in the soil profile. At *the 15th I nternational Conference Monitoring of G eological Processes and Ecological Condition of the Environment*. *European Association of Geoscientists & Engineers*, *2021*, 1–5. DOI: https://doi.org/10.3997/2214-4609.20215k2048

Sadeghi, M., & Zarshenas, P. (2022). Adsorption of Pb^{2+} Ions Aqueous Environment Using the Novel CaoCdo /Z sm^{-5} Zeolite Nanocomposite Adsorbent. *Journal of M aterials and Polymer Science*, *2*(1), 1–3. DOI: https://doi.org/10.47485/2832-9384.1004

Sydorchuk, O., Matsuska, O., Sabadash, V., & Gumnitsky, J. (2014). Parallel-serial adsorption of phosphate ions by na tural sorbents. *Eastern-European Journal of Enterprise Technologies*, *6* (6(72)), 56. DOI: https://doi.org/10.15587/1729-4061.2014.30874

Wang, Y., Liu, S., Pan, J., Zhang, H., Wang, B., & Yan, W. (2024). MER Zeolite with Remarkable Pb^{2+} and Cd^{2+} Removal Capability Cost-Effectively Synthesized from post-processed Natural Stellerite. *Inorganic Chemistry*, *64*(1), 393–403. DOI: https://doi.org/10.1021/acs.inorgchem.4c04717

Youssif, M. M., El-Attar, H. G., Hessel, V., & Wojnicki, M. (2024). Recent Developments in the Adsorption of Heavy Metal Ions from Aqueous Solutions Using Various Nanomaterials. *Materials*, *17*(21), 5141. DOI: https://doi.org/10.3390/ma17215141

Zhang, H., Jiang, X., Zhao, M., Ma , X., Yang, Y., & Li, T. (2024). Performance of ball-milling-modified coal gangue on Pb^{2+}, Zn^{2+}, and NH^{4+} –N adsorption. *Journal of Material Cycles and Waste Management*, *26*, 2115–2127. DOI: https://doi.org/10.1007/s10163-024-01947-1