

Characterization of adsorbents from Ukrainian kaolinite clay for the sorption of nickel: insight and practical application for water treatment in conditions of economic constraints

Yuliia Trach^{a,b}, Filip Bujakowski^c, Eugeniusz Koda^a, Łukasz Mazur^a, Krzysztof Nejbert^d, Anna Podlasek^a, Magdalena Daria Vaverková^{a,e,*}

^aInstitute of Civil Engineering, Warsaw University Life Sciences – SGGW, 02 776 Warszawa, Nowoursynowska 159, Poland, emails: magdalena.vaverkova@mendelu.cz/magdalena_vaverkova@sggw.edu.pl/magda.vaverkova@mendelu.cz (M.D. Vaverková), yuliia_trach@sggw.edu.pl (Y. Trach), eugeniusz_koda@sggw.edu.pl (E. Koda), Lukasz_mazur@sggw.edu.pl (Ł. Mazur), anna_podlasek@sggw.edu.pl (A. Podlasek)

^bDepartment of Water Supply, Water Disposal and Drilling Engineering, National University of Water and Environmental Engineering, Soborna 11, 33028 Rione, Ukraine

^cInstitute of Environmental Engineering, Warsaw University Life Sciences – SGGW, 02 776 Warszawa, Nowoursynowska 159, Poland, email: filip_bujakowski@sggw.edu.pl (F. Bujakowski)

^dFaculty of Geology, University of Warsaw, Żwirki i Wigury 93, Warszawa, 02–089, Poland, email: knejbert@uw.edu.pl (K. Nejbert)

^eFaculty of AgriSciences, Mendel University in Brno, Zemědělská 1, 613 00 Brno, Czech Republic

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ABSTRACT

Heavy metals are often present in mining waters. In this research, comparative studies of Ni²⁺ adsorption were made on natural red and white kaolins from the Murzyntski quarry in Ukraine. Red kaolin showed a higher adsorption capacity of Ni²⁺ and was more effective than white kaolin at pH 3.5 and pH 7.5, total dissolved solids (TDS) 0.01, 1.5, and 2.5 g/L. This was since red and white kaolins had different percentages of minerals in their composition, that is, kaolinite, quartz, and hematite, as well as different pH_{pzc} values. The adsorption capacity of saline water was tested for potential environmental applications of such materials in the purification of mining waters. To ensure the ecological and economic effect of applying the kaolins studied, it was proposed to introduce them into the Svistunova accumulation lake located about 150–200 km from the kaolin quarry.

Keywords: Ecological effect; Mining water; Adsorption; Nickel; Kaolin; Environmental applications

1. Introduction

Currently, the mining sector is facing increasing pressure to implement the principles of sustainable mining [1]. Mining is the extraction of geological material or other valuable minerals from the surface of the Earth or from its depths, mostly from an orebody. It strengthens and constitutes the basis for the industrial development of many countries [2]. Mining provides also economic and social development,

employment, and supply of basic raw materials to society, and supports economic, social, and infrastructural development in underdeveloped countries and areas [2,3]. The mined minerals have usually a high economic value for entrepreneurs but pose a negative impact on the surrounding environment [4,5]. Control and assessment of environmental impact are important in every industry, including the large-scale development of metallurgical mines [3,6,7]. The impact of mining activities on water pollution has been

* Corresponding author.

reported in numerous studies all around the world [2,8,9]. Groundwater contamination caused by acid mine drainage and leachate from neutralized mine waste is the most common cause of water pollution from mining [2,9,10]. Overall, acid mine drainage and the resulting release of potentially toxic elements are major problems for mining industries worldwide [11,12].

Among common purification techniques, adsorption has lately gained much attention because it is an eco-friendly, cost-effective, and simple operating technology. In recent years, much attention has been focused on the selection and/or production of low-cost adsorbents with good metal-binding capacities [13]. Many investigations in this field indicated zeolite as a cost-effective adsorbent because of its good metal-binding capacity, local availability in large quantities, simple operating technology, and general lack of secondary pollution [6,14–16] presented experimental data on the removal of ammonia by zeolite. The main disadvantage of using zeolites for such needs in Ukraine is their remote geographical location from the studied accumulation of lakes and old river beds [17]. In [17–20], adsorption properties of heavy metals (HM) by various volcanic tuffs and kaolins, as well as the dependence of their adsorption capacity on pH, temperature, and initial concentration of HM were studied. Much attention is also devoted to the assessment of the suitability of naturally occurring kaolin deposits as a raw material to produce synthetic zeolites which are materials with better sorption parameters concerning to specific groups of pollutants [21]. Synthetic kaolin-based zeolites are increasingly used to soften industrial water and remove metals. The suitability of kaolins from individual deposits to produce this type of zeolite depends particularly on the composition of the base rock [22].

Kaolins represent clays that are very common in Ukraine. Their value is determined by the peculiarity of physical-chemical properties and the scale of their use in almost all industries. Due to the significant content of alumina – up to 40% – kaolin is the main component of mixtures to produce porcelain, faience, sanitary ware, and building ceramics. High whiteness and excellent composition make kaolin an irreplaceable raw material and the main filler in the production of paper and cardboard in metallurgical, ceramic, cement, and other industries. Not all kaolin clays are white. Some of them are reddish-brown due to the presence of iron. In such cases, kaolin may not be suitable to produce paper, earthenware, cement, etc.

In the natural environment, clay minerals play the role of natural scavengers by filtering out pollutants from water through both ion exchange and adsorption mechanisms. Clays consist of extremely fine particles which exhibit chemical properties of colloids [23]. Their high specific surface areas, the chemical, and mechanical stability, layered structures, high cation-exchange capacity, and the presence of Brønsted and Lewis acidity on their surfaces [24] make clays potentially excellent adsorbent materials [7,25].

There are numerous scientific reports on experimental studies dealing with the adsorption of heavy metals by kaolins, performed in acidic and weakly alkaline waters [18,25,26]. One of the important factors that may influence HM adsorption by kaolin is total water mineralization. There is a lack of precise data on the relationship between the HM

sorption capacity in acidic and weakly alkaline water with different total dissolved solids (TDS) values and the mineral composition of kaolins. In the experiments, Ni^{2+} was used as a HM in the experiments for it is considered a representative of heavy metals which often occur in all waters of mining/metallurgic industries [14,27–29].

Taking the above issues into account, this research was focused on determining the mineralogical composition of red and white kaolins from one quarry. Based on the obtained results, it was essential to test the relationship between their sorption capacity in acidic water and weakly alkaline water (with different TDS values) and determine its dependence on the mineralogical composition.

The study also aimed at assessing the influence of doses of red and white kaolins on the sorption process efficiency. This is indispensable in determining the economic effect of their application. To ensure the ecological and economic effect of using the kaolins from Ukraine it was essential to search for accumulation lakes of mine waters located in the close vicinity of kaolin quarries [30,31].

The presented research should allow for the development of an effective technological key for the reclamation of water reservoirs in mines in the Krivbas Basin with the use of red kaolins, previously treated as industrial waste and subjected to landfilling.

2. Geological setting of kaolin deposits in Ukraine

Ukraine is one of the main kaolin producers in the world [32]. The largest kaolin deposits of the Ukrainian Shield stretch over 950 km from Polissya to the Azov Sea in an up to 350 km wide belt. The origin of kaolin deposits in Ukraine is related to the weathering of Precambrian crystalline rocks which are rich in feldspar. These rocks are represented by granites, gneisses, and mafic rocks that contain large amounts of plagioclase. Kaolin deposits can be classified into two types: weathering, including most of the documented deposits, and hydrothermal-metasomatic ones which occur only in the Berehivskiy kaolin region [32,33]. Due to sedimentation processes occurring during the weathering of feldspar-rich rocks, kaolin deposits are subdivided into primary (kaolin-rich weathering occurs *in situ*, directly above the weathered rocks) and secondary, in which the weathering kaolin was transported and deposited within the lowlands of the Ukrainian Shield and its slopes. The Murzynski deposit, from which the analysed samples were collected, is classified as a secondary kaolin deposit.

Kaolin secondary deposits in Ukraine are characterized by a variable thickness ranging from 4 m to even 20 m. The mineralogy and chemical composition of kaolin raw materials are variable. The main components are kaolinite, quartz, iron hydroxides, and heavy minerals represented by zircon, tourmaline, rutile, magnetite, ilmenite, anatase, monazite, and others [30,31]. The quality of kaolin raw material is significantly affected by the presence of Fe_2O_3 and TiO_2 impurities. High-iron ($\text{Fe}_2\text{O}_3 > 0.5\%$), low-iron ($\text{Fe}_2\text{O}_3 < 0.5\%$), titanite ($\text{TiO}_2 > 0.5\%$), and low-titanite ($\text{TiO}_2 < 0.5\%$) kaolin raw materials have been distinguished regarding the Fe and Ti contents in raw kaolin.

The content of alumina (not below 40% in the best varieties) and iron oxide (not more than 1.5%) plays an

important role in determining kaolin value for the ceramic industry. Low grades of kaolin, that is, those with a low alumina content, are used to produce ceramic tiles, as an alumina additive for cement manufacture, etc. Kaolin strongly enriched with iron oxyhydroxides, distinguished as red kaolin, can potentially be a good and cheap raw material also used in technologies for the removal of HM from mining wastewaters.

In Ukraine, accumulating lakes of mine waters from the Kryvyi Rih iron ore basin (Kryvbas) (Fig. 1) is the closest (less than 100–200 km) to the kaolin quarry. Annually, mining enterprises in the city of Kryvyi Rih (Kryvyi Rih iron ore basin) pump out about 40.0 million m³ of groundwater. Of these, 17–18 million m³ represent mineralized mine water, most of which accumulates in the Svistunova mine water storage reservoir. In the autumn–winter season, such waters are discharged into the Ingulets River. In this region, there are 40 streams of which 67.5% are right-bank and 1/3 left-bank concerning to the Ingulets River. According to Sherstyuk and Serduk [31], the water of these lakes always contains high concentrations of Cu, Ni, Zn, Pb, Fe, and Mn. These elements enter the water through the discharge of water polluted by mining operations. In addition, the area is characterized by strong north-eastern winds which contribute to the transfer of a certain percentage of sedimentary material with accumulated heavy metals [30]. Further downstream, waters of the Ingulets R. flow into the Dnieper, Ukraine's largest river. Originally, the Dnieper was a meandering river with local traces of braiding. Currently, due to the construction of the Dnieper cascade system, it is divided into a number of dam reservoirs. In such cases, heavy metals of anthropogenic origin tend to have significant concentrations in the river alluvia [34]. In addition, the forehead of the water reservoir

is a barrier to the movement of suspended sediment, causing increased pollutant concentrations in contemporary alluvium.

3. Methods and materials

3.1. Material used in the study

The material used in the study was sampled from the Murzyntski kaolin deposit located in central Ukraine (49°08'10.0"N 30°55'16.0"E). Two samples of loose kaolin samples, with a mass of 0.5 kg each were taken for examination; they represented the red (sample R-K) and white (sample W-K) kaolin raw material which was macroscopically distinguishable in the mine excavation (Fig. 2). Each standardized sample was subdivided by mixing and quartering into smaller, representative portions enabling the performance of Ni²⁺ adsorption tests by white and red kaolin under various experimental conditions.

3.2. Chemical and mineral composition of kaolin samples

The chemical composition of two representative kaolin samples was determined using X-ray fluorescence (XRF). Chemical analyses were performed with the ARL Advant'X IntelliPower 1200 apparatus (Thermo Fisher Scientific, Waltham, MA, USA) using the X-ray spectral analysis. Loss on ignition (LOI) was determined by weight loss after heating the samples at 950°C. The mineral composition of white and red kaolin samples was determined by powder X-ray diffraction using the Marvel X-ray diffractometer (Malvern Panalytical, Malvern, UK). To precisely determine the amount of main rock-forming minerals

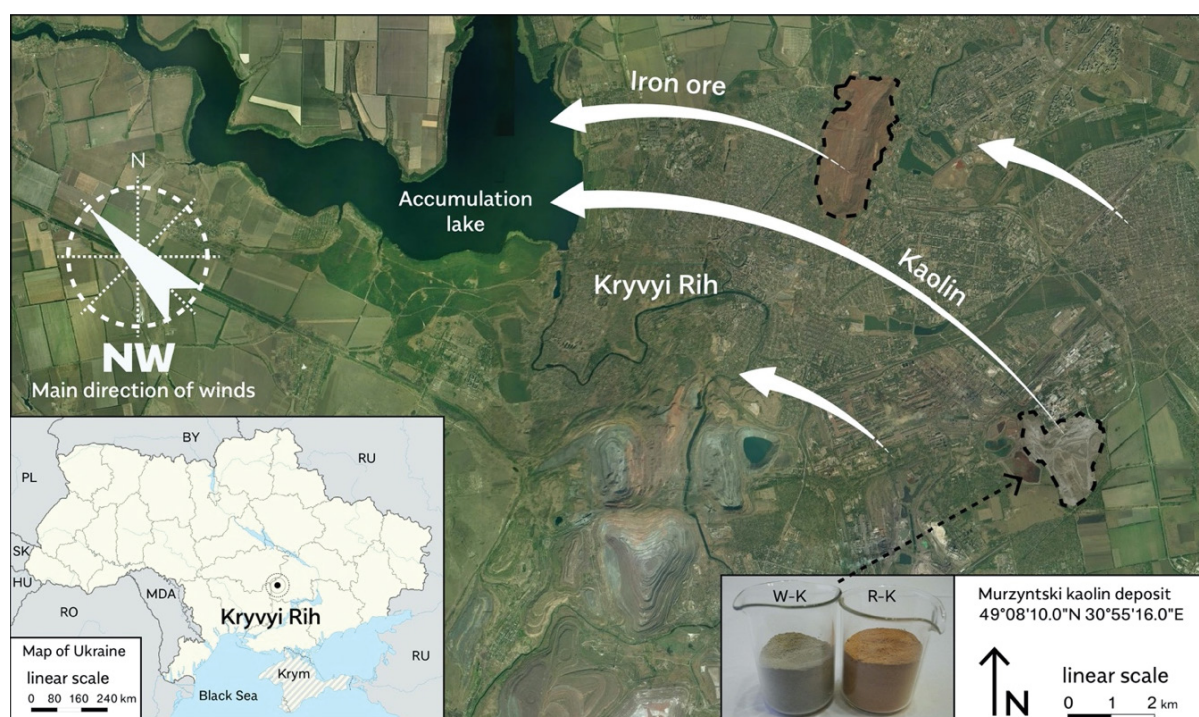


Fig. 1. Location of Kryvyi Rih (Ukraine) with the accumulation lakes.



Fig. 2. Kaolin samples from the Murzyntski deposit (a) W-K and (b) R-K.

(kaolinite, quartz, mica, feldspar, and other minerals), the samples were recorded within a range of 5° – 65° 2θ , at a step width of 0.022° 2θ , 2.1 step/s. Diffraction experiments were performed for averaged powder preparations, which were placed in a holder and pressed under conditions ensuring a high degree of disorientation of individual mineral grains. During the recording of the diffraction data, $\text{CoK}\alpha$ radiation was used, generated from an X-ray tube supplied with a current of 7.5 mA. The total measurement time for a single sample was approximately 22 min. The results obtained were processed using the X Pert High Score Plus software (ver. 2.2e) with the ICDD PDF-2 Release database RDB 2008. The X-ray diffraction (XRD) examination was performed in the X-ray laboratory.

3.3. Determining the point of zero charge

The point of zero charges (PZC), pH_{pzc} for the white and red kaolins was determined using the titration method [18,35]. Accordingly, the kaolin samples of air-dried material (0.2 g) were shaken in PVC vials for 24 h. The volume of solids was 40 mL with 0.01 and 0.1 mol/L KNO_3 . Correction pH values were obtained by adding KOH or HNO_3 solutions (0.1 mol/L) for the range 2.0–11.0. Determination of the point of zero charges was done twice, and the obtained values were averaged. The natural materials were dried at 105°C to a constant weight and ground to a grain size below 0.01 mm.

3.4. Adsorption experiments

The adsorption equilibrium experiment was carried out in conical flasks by shaking the R-K and W-K samples in

Ni^{2+} solutions at 20°C . It is traditionally accepted to accept the contact time of heavy metals with the adsorbent as 24 h. The Ni-solutions were obtained by dissolving $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ in water characterized by different TDS values (0.01, 1.0, and 2.5 g/L). The solutions were characterized by Ni^{2+} concentrations ranging from 2.5–17 mg/L, $\text{pH } 3.5 \pm 0.08$, and $\text{pH } 7.5 \pm 0.08$. Studies of Ni^{2+} adsorption by R-K and W-K samples included two types of experimental series. The first of them was a study of the dependence of adsorption capacity on the kaolin mass. The Ni^{2+} solution was prepared with a concentration of 17 mg/L. The solutions were prepared to plot isotherms of Ni^{2+} sorption. The maximum actual concentration of Ni^{2+} was 17 mg/L solutions. When planning studies on the dependence of Ni^{2+} sorption capacity on the dose of kaolins were taken in the range 0.2 to 6.14 g/L. Therefore, the authors decided to use a solution with the highest concentration of 17 mg/L for such a study. It was assumed that this would allow determining the concentration of Ni^{2+} , after its sorption, using one plotted calibration graph for ASS. The R-K and W-K samples with a mass ranging from 0.2–6.14 g/L were then added to the prepared solution. After shaking, each solution was separated from the mixtures by centrifuging for 5 min at 8,000 rpm. The Ni^{2+} concentration in the solutions before and after the adsorption was measured using the AAS technique using the PG Instruments spectrometer. In the solutions, pH was measured using a multimeter. All experimental studies were made in triplicates. The obtained results were presented as means of arithmetic values for the respective parameters.

Equilibrium adsorption capacity q_e (mg/g) was calculated according to Eq. (1):

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where: C_0 (mg/L) and C_e (mg/L) are Ni^{2+} concentrations in the solution before adsorption and in the equilibrium state, respectively, V (L) is the volume of Ni^{2+} solution, and m (g) is the mass of the kaolin sample.

Data obtained from the adsorption experiment were treated using the Langmuir and Freundlich non-linear models [17]. Regression was used as the applied isotherm equation [17,18]. Such models are usually used to describe experimental points and determine the maximum adsorption capacity (q_{\max}). The model which fits best the experimental data is determined by calculating and comparing the maximum value of standard deviation R^2 for each model. Calculations of q_{\max} and coefficient R^2 were carried out in Excel using Solver.

4. Results

4.1. Chemistry and mineralogy of kaolin samples used in the experiments

The results of mineralogical studies are confirmed by geochemical data (Table 1), which point out high SiO_2 and Al_2O_3 contents ranging from 49.62–48.45 wt.% and 31.38–35.70 wt.%, respectively. The only significant difference in the chemical composition was an almost three times higher content of Fe_2O_3 in the red kaolin sample. The contents of other elements were at comparable levels (Table 1).

The R-K and W-K raw materials have similar mineral compositions (Fig. 3). Both samples are characterized by very high kaolinite contents (89.4 and 87.0 wt.% by weight), and quartz (7.0% and 13.0%), respectively. Hematite was identified in the R-K sample at 3.6%. Small amounts of calcite, anatase, and magnetite were also identified in the analysed samples.

Table 1
Chemical composition of the examined R-K and W-K samples determined by XRF analysis

	R-K	W-K
LOI at 950°C	13.45	12.97
SiO_2	49.62	48.45
Al_2O_3	31.38	35.70
Fe_2O_3	3.64	1.14
CaO	0.35	0.17
MgO	0.23	0.09
SO_3	0.12	0.02
K_2O	0.15	0.35
Na_2O	0.04	0.14
Cr_2O_3	0.013	0.017
TiO_2	1.307	0.842
Mn_2O_3	0.02	0.012
P_2O_5	0.04	0.029
SrO	0.009	0.01
ZnO	0.01	0.009

4.2. Point of zero change for R-K and W-K samples

The plot for the determination of PZC in the R-K and W-K samples is shown in Fig. 4. It is shown as a function of initial pH values (pH_i) of solutions from the pH values of filtered solutions (pH_f) after equilibration, that is, after 24 h of their contact with R-K and W-K. The PZC of R-K and W-K samples in 0.01 and 0.1M KNO_3 aqueous solutions was at pH 8.2 and 6.5, respectively (pH level at which a plateau is obtained; Fig. 4).

4.3. Influence of the amount of R-K and W-K samples on the adsorption capacity of Ni^{2+}

In the next step, a dose of 0.2 g/dm³ of R-K and W-K each was taken. The ability of R-K and W-K to remove Ni^{2+} from aqueous solutions was studied for various adsorbate concentrations by applying different amounts of the adsorbent. Experimental studies showed that the adsorption capacity of Ni^{2+} depends on the R-K and W-K mass in distilled water (Fig. 5). The Ni^{2+} concentration was measured before and after the adsorption using adsorption capacity (q , mg/g) which was decreasing with the increasing initial amount of clay used in the system. The experiments were carried out in distilled water at pH 3.5 and pH 7.5. The maximum adsorption capacity of Ni^{2+} was achieved in aqueous solutions using 0.2 g/L R-K at pH 3.5. Therefore, in the next step, a dose of 0.2 g/L of R-K and W-K each was taken.

4.4. Determination of the maximum adsorption capacity of Ni^{2+} on R-K and W-K samples

An example of experimental Ni adsorption onto red kaolin isotherms at pH 3.5, doses 0.2 g/L and TDS 0.01, 1.5 and 2.5 g/L, and dependencies non-linearized according to Langmuir and Freundlich equations are shown in Fig. 6.

The Langmuir and Freundlich models were used to determine the type of adsorption mechanism and q_{\max} of Ni^{2+} for R-K and W-K samples in water. The values of q_{\max} of Ni^{2+} by R-K and W-K and calculation of R^2 , at initial concentrations in the range of 2.5–17 mg/L, pH 3.5 and pH 7.5, TDS 0.01, 1.5, 2.5 g/L of water, are presented in Table 2.

R-K and all TDS values exhibited a lower uptake towards Ni^{2+} ions at pH 7.5 than at pH 3.5. Similar dependencies were observed for the adsorption of Ni^{2+} by W-K at the same water parameters.

The performed analysis allows to draw the following conclusions. The highest R^2 values correspond to the adsorption of Ni^{2+} by both kaolins following the Langmuir model. The adsorption of Ni^{2+} by both kaolins was of monolayer type. This may be related to greater homogeneity of the active adsorption sites on the R-K and W-K samples, and the absence of a wide variety of mineral phases. Even though the studied kaolins were not monophasic in mineralogical composition, the modelling showed a monolayer type of Ni^{2+} adsorption. This can be explained by the fact that the presence of quartz (SiO_2) in both kaolins did not participate in the adsorption of Ni^{2+} , and the effect of hematite presence in R-K (3.6%) was not significant.

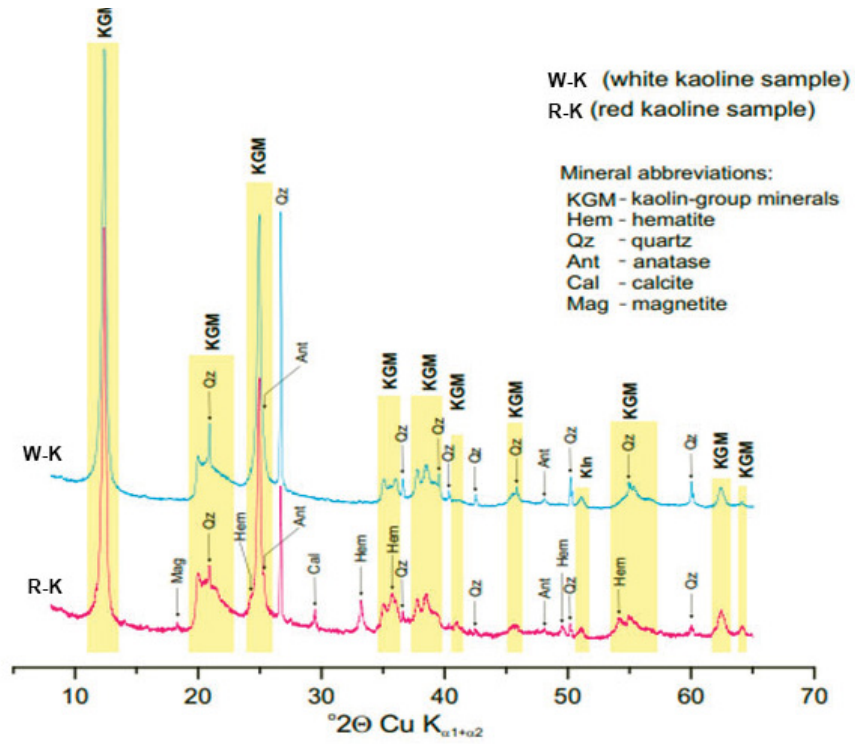


Fig. 3. X-ray diffractograms for R-K and W-K samples.

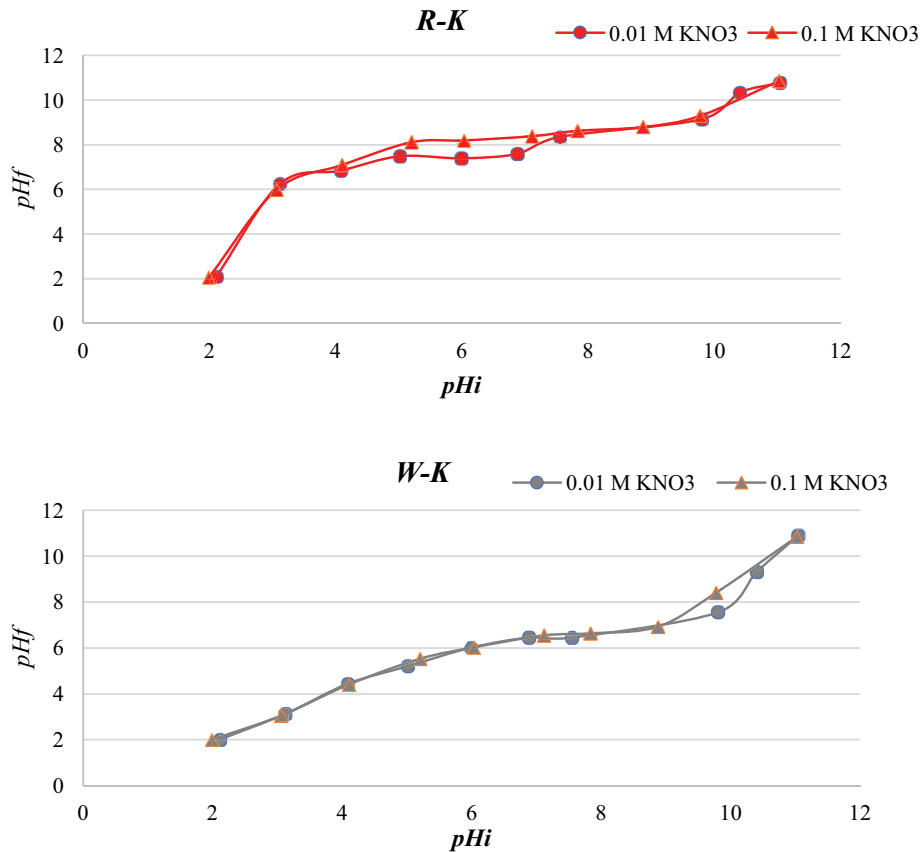


Fig. 4. Determination of $pH_{f,pzc}$ for R-K and W-K samples in KNO_3 solutions.

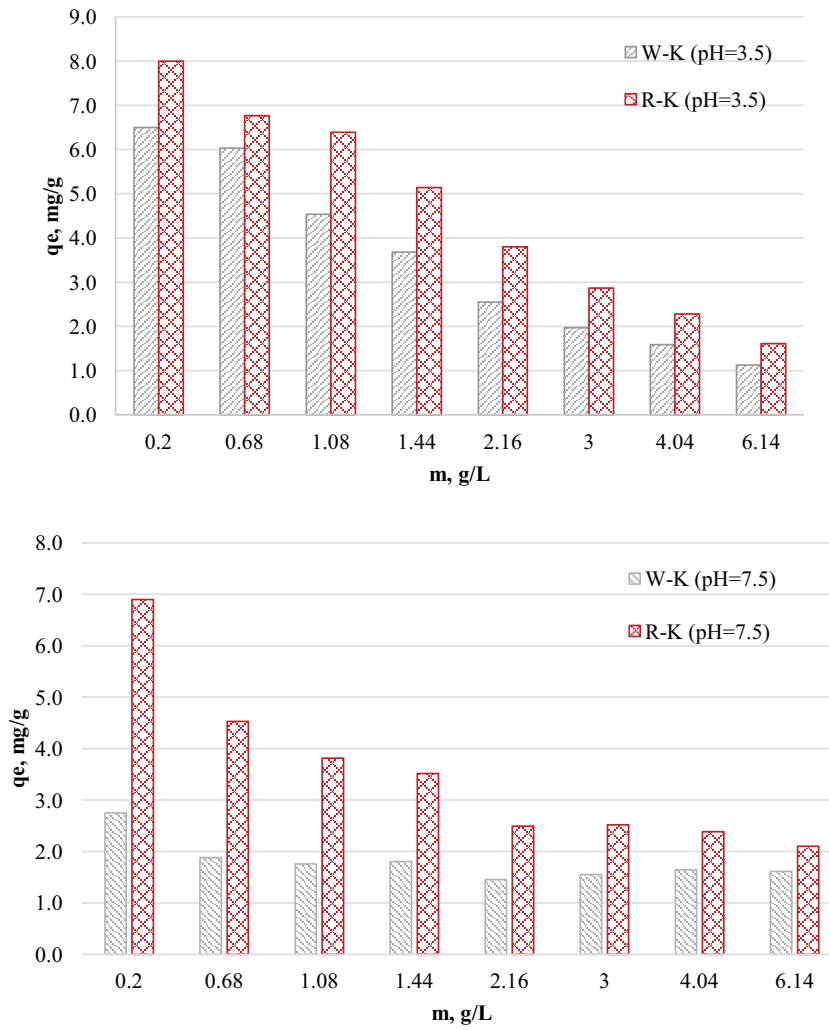


Fig. 5. Dependence of the adsorption capacity of Ni²⁺ on the R-K and W-K mass in distilled water.

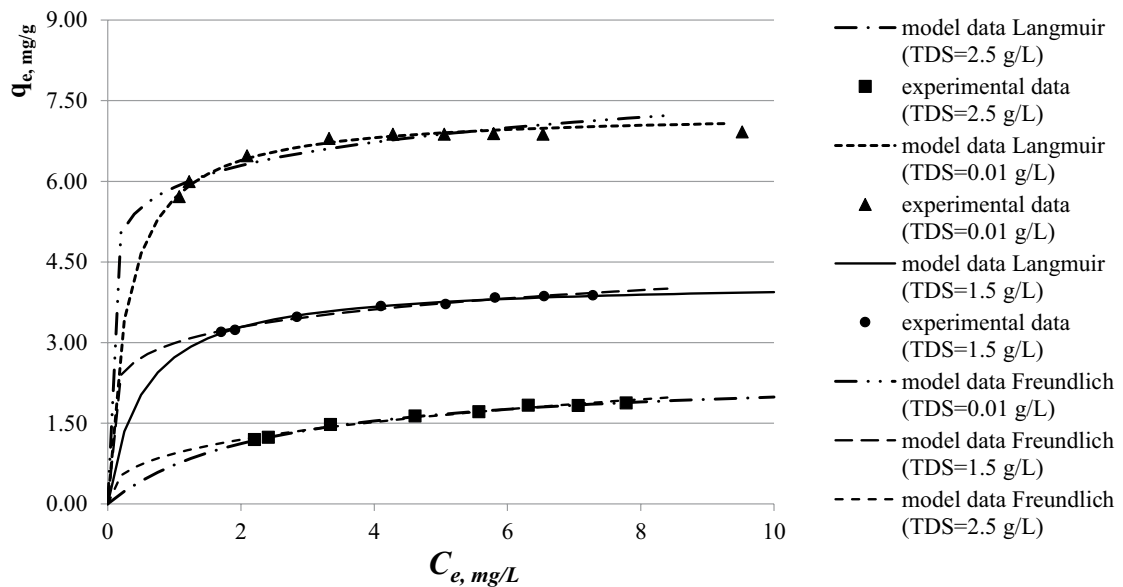


Fig. 6. Langmuir and Freundlich isotherms for Ni²⁺ adsorption onto red kaolin.

Table 2
Values of standard deviation R^2 and maximum adsorption capacity of Ni^{2+} at different initial water parameters

Natural sorbent	pH	TDS	Langmuir	Freundlich	q_{\max}
		g/L	R^2	R^2	mg/g
R-K	3.5	0.01	0.996	0.991	6.9
		1.5	0.995	0.987	4.6
		2.5	0.991	0.990	2.9
R-K	7.5	0.01	0.993	0.986	4.2
		1.5	0.989	0.982	2.4
		2.5	0.977	0.977	1.9
W-K	3.5	0.01	0.994	0.987	5.9
		1.5	0.991	0.989	3.6
		2.5	0.986	0.984	1.8
W-K	7.5	0.01	0.995	0.991	3.1
		1.5	0.989	0.982	1.4
		2.5	0.987	0.987	0.9

4.5. Influence of water pH, Eh, and TDS on the adsorption capacity of Ni^{2+} by R-K and W-K samples

The study of the possibility of using R-K and W-K for the adsorption of Ni^{2+} , included a comparison of changes in the basic water parameters, that is, pH, Eh, and TDS before and after the adsorption. Results of determining these water parameters at R-K addition (initial Ni^{2+} concentration 2.5–17 mg/L, pH 3.5, TDS 2.5 g/L) are presented in Fig. 6. After adding R-K, the water pH increased $\Delta\text{pH} = 1.5$ –1.82. A similar increase of water pH was observed at TDS 0.01 and 1.5 g/L, attaining $\Delta\text{pH} = 2.5$ –2.96 and $\Delta\text{pH} = 1.95$ –2.26 respectively. However, the addition of W-K to water at the same initial parameters did not change its pH. Therefore, R-K can be used to partially neutralize acidic water of varying salinity.

Studies of pH changes after R-K and W-K addition (initial pH = 7.5, TDS = 2.5 g/L) showed that R-K did not change the water pH. Similar results were obtained by adding R-K and W-K to water characterized by pH = 7.5, TDS = 0.01, and 1.5 g/L. This suggests that the adsorption of Ni^{2+} ions occurred mainly on the surface of the dominant mineral kaolinite and not through the mechanism of ion exchange when alkaline ion-exchange metals pass into the water and increase the water pH.

An important water parameter that may change after adding natural sorbents is Eh. Thus, its reduction was always observed after adding R-K and W-K to water (initial pH = 3.5 and TDS = 0.01, 1.5, and 2.5 g/L). Eh decrease was approximately the same: $\Delta\text{Eh} = -110$ mV at TDS 0.01 g/L, $\Delta\text{Eh} = -80$ mV at TDS 1.5 g/L, and $\Delta\text{Eh} = -40$ mV at TDS 2.5 g/L. Eh change before and after the adsorption of Ni^{2+} by R-K at pH = 3.5 and TDS = 2.5 g/L is shown in Fig. 7.

Water TDS was determined before and after the Ni^{2+} absorption by R-K and W-K samples. The results indicate that the TDS value did not change after 24 h (at initial pH = 7.5). However, when comparing the change before and after the adsorption of Ni^{2+} by both kaolins, the TDS value of acidic water (pH = 3.5, at all initial TDS) decreased. The result of the experimental study is presented in Fig. 7. Thus, the decrease

of TDS of acidic water (pH = 3.5) and a higher adsorption capacity of Ni^{2+} by the studied kaolins can be explained as follows. Low water pH and the respectively increased concentration of H^+ ions lead to partial destruction of the kaolinite crystal. The result was an increase in the surface area of kaolinite, which was able to adsorb more Ni^{2+} ions. The results of our experimental studies are consistent with the studies conducted by the authors [37].

5. Discussion

Experimental studies demonstrated that the dominant mineral of the R-K and W-K samples is kaolinite. The fundamental difference in the mineralogical composition between the studied kaolins is the percentage composition of kaolinite, quartz, and hematite.

Kaolinite is formed as a result of the chemical weathering of aluminosilicates, especially feldspars [38,39]. The chemical formula of kaolinite is $\text{Al}_4[\text{Si}_4\text{O}_{10}][\text{OH}]_8$ or $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$. The crystalline structure of kaolin comprises infinite layers of silicic acid tetrahedrons, distributed along its outline and aluminohydroxyl octahedral. The packets are interconnected and occur very close to each other, due to which the mineral (kaolin) does not swell in water. Moreover, a small amount of cation-exchange metals occurs in the kaolinite crystal.

In the kaolins studied, the cation-exchange capacity (CEC) of kaolinite was low and primarily confined to the surface, in contrast to other groups of clay minerals, such as smectites and illites, where a large part of the CEC was associated with interior sites [40,41]. Hence, kaolinite is an ideal material to study the purely surface adsorption processes. Sources of surface charge are hydroxyl groups located on the lateral cleavages of kaolinite, which are capable of protonation–deprotonation reactions [42]. Broken bonds and M–OH bonds along the surfaces of clay crystals result in hydrolysis [43].

Thus, the results of experimental determination of pH_{pzc} of the tested R-K and W-K samples with a similar mineralogical and chemical composition of kaolins from the same quarry, indicate that they have different pH_{pzc} values. Thus, these kaolins can have different characteristics as HM sorbents. Such results are consistent with the identified pH_{pzc} values of minerals that compose the kaolins: 6.5–8.5 for hematite, below 5 for quartz, 3.0 for kaolinite [41–44]. The value of pH_{pzc} for aluminosilicates usually depends on the Al_2O_3 content in the mixture of SiO_2 and Al_2O_3 .

The studies showed the dependence of the amount of adsorbed Ni^{2+} in equilibrium on the kaolin mass. The amount of adsorbed Ni^{2+} decreased with the mass increase in both kaolins. The presence of a large amount of kaolin significantly reduced the unsaturation of adsorption sites; the number of such areas per mass unit decreased and led to relatively lower adsorption [45]. This is not surprising, since, at a fixed initial concentration of a solute, the increasing amount of adsorbent does not always increase the adsorption capacity. However, the increased amount of adsorbents can provide a larger surface area and, accordingly, more sites for adsorption.

Consequently, the increased amount of kaolin at the solid/liquid interface has a significant effect on the adsorbate–adsorbent interaction. This may be due to the screening effect

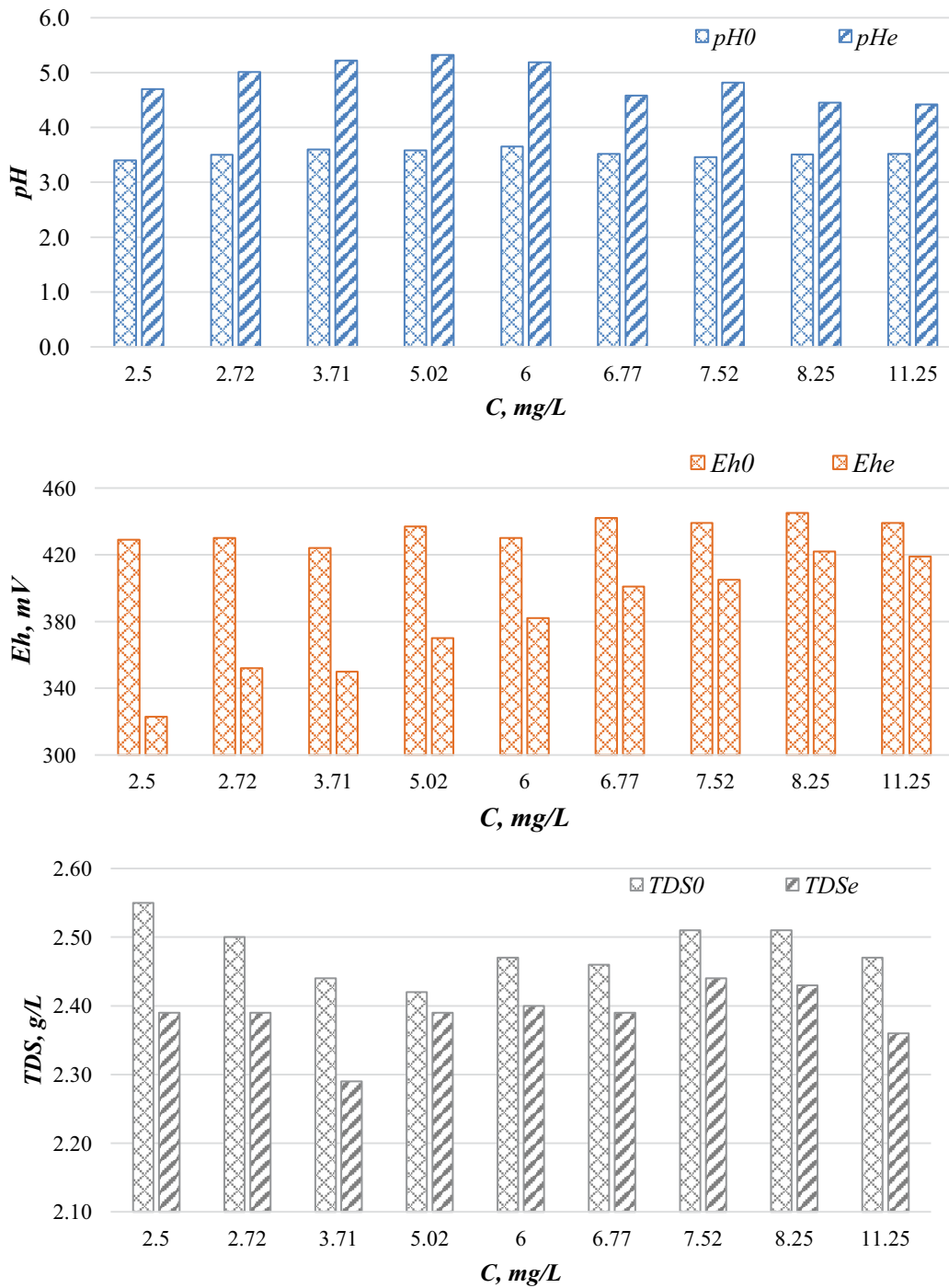


Fig. 7. Change of pH, Eh, TDS before and after the adsorption of Ni²⁺ by R-K at initial pH = 3.5 and TDS = 2.5 g/L.

of the electrostatic interaction between the adsorbate and the adsorbent (HM and negatively charged adsorption sites) [46]. In addition, as presented in [25], an increased HM concentration can also reduce the interface potential and thickness of the electric double layer, reducing electrostatic adsorption. Similar experimental results were obtained [17,47].

Clay minerals, namely kaolin, in an acidic medium can exchange cations with H⁺ ions and leach Al³⁺ and other cations from both tetrahedral and octahedral regions, which

leads to the destruction of mineral crystals [48,49]. The research [50] informed that this process as a rule increases the surface and acidity of clay minerals due to the partial dissolution of outer layers. The crystalline structure of kaolinite is transformed into amorphous metakaolin in acidic water. Octahedral Al³⁺ ions are preferentially released from the clay structure leading to the formation of additional Al-OH and Si-OH bonds without affecting the original mineral structure [51].

Table 2
Values of standard deviation R^2 and maximum adsorption capacity of Ni^{2+} at different initial water parameters

Natural sorbent	pH	TDS	Langmuir	Freundlich	q_{\max}
		g/L	R^2	R^2	mg/g
R-K	3.5	0.01	0.996	0.991	6.9
		1.5	0.995	0.987	4.6
		2.5	0.991	0.990	2.9
R-K	7.5	0.01	0.993	0.986	4.2
		1.5	0.989	0.982	2.4
		2.5	0.977	0.977	1.9
W-K	3.5	0.01	0.994	0.987	5.9
		1.5	0.991	0.989	3.6
		2.5	0.986	0.984	1.8
W-K	7.5	0.01	0.995	0.991	3.1
		1.5	0.989	0.982	1.4
		2.5	0.987	0.987	0.9

The results of experimental studies, which are presented above, allow to draw the following conclusions. Adding R-K and W-K to acidic (pH 3.5) and weakly alkaline (pH 7.5) water changed the main physical and chemical parameters of water and its pH, Eh, and TDS. Even though the R-K and W-K samples have similar chemical and mineralogical compositions, they do not change the same water parameters. This is mainly due to the peculiarity of the crystal structure of the dominant mineral kaolinite and hematite present in the samples. The contact of W-K with acidic water did not increase the water pH value. An increase in the water pH was observed upon the contact of R-K with acidic water. This can be explained by the influence of the suspended composition of hematite, the pH_{pzc} value of which is 8.5 in most cases.

As shown above, the application of both kaolins in reducing HM, that is, Ni^{2+} , and improving the quality of water in general, is associated with a decrease in the value of water Eh, after the contact of both kaolin samples with water. A decrease of this indicator was observed in water at all initial values of pH (3.5 and 7.5) and TDS (0.01, 1.5, and 2.5 mg/L).

The experiments carried out to study the mechanism of Ni^{2+} adsorption by R-K and W-K kaolins using the Langmuir and Freundlich models showed the following. The obtained adsorption isotherm and calculated values of R^2 coefficients indicated that adsorption in water characterized by TDS at 0.01, 1.5, and 2.5 g/L, and pH 3.5 and pH 7.5 occurred according to the Langmuir model. This corresponds to the existing data on the structure of the kaolinite crystals; the adsorption of heavy metal cations occurs only on their surfaces. The adsorption capacity of Ni^{2+} for the optimal doses of R-K and W-K samples at 0.2 g/L was in all cases higher for the red kaolin.

The papers [26–28] presents experimental data about adsorption capacity HM by kaolins. The adsorption capacity of Ni^{2+} was 10.4 mg/g onto kaolin. The adsorption capacity was studied in distilled water, but the kaolin itself was chemically modified. The results of dependence of Ni^{2+} sorption capacity on the dose of kaolin is also presented. The resulting dependencies were consistent with the dependencies obtained during our research.

The highest commercial value is characterized in W-K by the iron content lower ($\text{Fe}_2\text{O}_3 < 2.5\%$) [52] than in R-K. Comparative experimental studies of W-K and R-K properties as heavy metal adsorbents in a case study of Ni^{2+} indicated that R-K has better properties than W-K for the reclamation of saline mining water in an accumulation lake.

The studies showed that the red kaolin in which Fe_2O_3 is at 3.5% has better characteristics in terms of its possible use for the rehabilitation of reservoir water affected by mining than W-K. In addition, a significant advantage of R-K use is also the fact that it can adsorb HM in both acidic and slightly alkaline aqueous media because its pH_{pzc} is below 8.5. The mining industry faces a challenge to choose reliable and cost-effective methods of water treatment from accumulation lakes. R-K samples in the form of dispersed powders in predetermined doses can be used as HM sorbents by direct introduction into the water, for example, in lakes or ponds. Together with the HM, they will settle to the bottom, remain there, and keep the HM in a stable form. Water in accumulation lakes may have different properties, for example with pH ranging from below 4 to over 7.5. The pH generally depends on the periods of heavy precipitation and snow melting. HM are almost always present in mining-impacted waters [4–11]. These pollutants enter the lake being washed out or carried by the wind from the HM-enriched slag dumps of metallurgical plants. Such phenomena are observed almost all over the world [53,54].

Comparative experimental studies of the adsorption capacity of Ni^{2+} by R-K and W-K samples were carried out under static conditions. Thus, these results can be applied to reclaim lake water with different pH values and total salinity.

The obtained results should become a basis for further research on the possibilities of the sorption of other HM occurring in waters pumped from the industrial district in Kryvyi Rih.

Obtaining a comprehensive view of the sorption capacity of red kaolin will allow to determine economic and ecological efficiency indicators in, the proposed to develop, key of industrial implementation.

When developing a financial plan of the endeavour, including namely the profit and loss account and balance sheets, which constitute a component of the economic efficiency analysis, it seems necessary to consider the effects of synergies. These synergies should cover the simultaneous reclamation of mining wastewater reservoirs.

6. Conclusions and recommendations

The presented study is focused on the impact of kaolin mineralogy, kaolin doses, and water total dissolved solids on the adsorption capacity of Ni^{2+} . It is concentrated on analysing the influence of kaolin mineralogy and doses on the adsorption capacity of Ni^{2+} in acidic and alkaline water (at different mineralization values). The main conclusions are as follows:

- X-ray diffraction analysis of white and red kaolin samples indicated that they contain more than 85% of aluminosilicate – kaolinite. The difference between the mineralogical composition of white and red kaolins is

that the red kaolin contains 3.6% hematite (which results in its red colour).

- It was experimentally determined that the pH_{pzc} of red kaolin is higher than the pH_{pzc} of white kaolin ($8.2 > 6.5$). This suggests that these two types of kaolin are capable of adsorption in acidic and slightly acidic aqueous media. Red kaolin is capable to adsorb pollution in alkaline waters.
- It was established that the Ni^{2+} adsorption capacity of red and white kaolins depends on their mass. In a certain value range, with the increasing kaolin dose, the adsorption capacity decreases. This is mainly due to the saturation of kaolin surfaces and their electrostatic mutual repulsion in water (negatively charged kaolinite particles), which covers the site for Ni^{2+} adsorption.
- The analysis of the calculated R^2 coefficient showed that the adsorption of Ni^{2+} by red and white kaolins occurs according to the Langmuir model and the adsorption of Ni^{2+} is of a monolayer type.
- Adsorption of Ni^{2+} by both kaolins is possible both in distilled water and in water characterized by total dissolved solids 2.5 g/L. The value of adsorption capacity depended on water total dissolved solids; the adsorption capacity of Ni^{2+} decreased with its increase, but it may be used to treat mining-impacted waters in reservoirs.
- To ensure the ecological and economic effect of using the investigated kaolins, it was determined that the accumulation lakes of mine waters from the Kryvyi Rih iron ore basin (Kryvbas), Ukraine are most closely located to the kaolin quarries.
- The synergy effect, including the simultaneous management of the material stored in heaps, and its direct application for reclamation of mine water reservoirs, enforces the use of the proposed concept interchangeably or predominantly concerning the use of organic sorbents and zeolites.
- Regarding the chemical composition of mining waters in the vicinity of the studied kaolin quarry ($\text{pH}_{\text{pzc}} > 7.5$), a possible using of white kaolin or other potential natural sorbents, namely zeolite, is excluded. Using the most popular natural Ukrainian zeolite sorbent, the deposits of which are concentrated in the western part of Ukraine has a number of disadvantages. Crucial is the geographical location of the working quarry (over 1,200 km), the need for additional mechanical grinding, and most importantly its pH_{pzc} of approximately 6.5–6.8.
- In order to develop the technological key, it seems necessary to conduct more extensive research on the sorbent properties of red kaolin in relation to other pollutants.
- Transition is recommended to the 5th stage of Technology Readiness Level (TRL) which concerns the validation of the developed prototype in an environment similar to the real one, on larger samples under conditions of a system imitating the real system.

In conditions of adapting the economy of Ukraine as a “Candidate Country” to the European Union, the proposed research can be treated as an initiative to support the creation of the concept of sustainable development understood as the improvement of economies in terms of the effective use of resources.

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