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Removal of cationic and anionic pollutants from water solutions using Ukrainian limestones: a comparative analysis

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ABSTRACT

Removal of cationic and anionic contaminants from surface waters with the same natural material is relevant both from environmental and economic points of view. Cationic contaminants can be removed by adsorption, while anionic ones – by the formation of insoluble calcium salts. In this study, nickel was taken as an example of a cationic pollutant and phosphate – an anionic pollutant. To test the removal efficiency of these substances, natural limestone and dispersed, thermally activated limestone were compared. Dispersed, thermally activated limestone gave better results of Ni^{2+} and PO_4^{3-} removal from all water solutions than natural limestone. This was due to its dispersion and subsequent heating to 240°C–250°C. As a result, limestone was destroyed and the calcite crystals broke apart. The doses of limestone were 2.0 and 4.0 g/L, the initial pH was 5 and 7, and the total dissolved solids (TDS) was at 0.02 and 0.55 g/L. Measurements of changes in the pH, Eh and TDS values were carried out. At water pH increase, the efficiency of Ni^{2+} removal decreased, while the efficiency of PO_4^{3-} removal increased. For purification of surface water by limestone, the selection of its type and dose depends on the usage of the water body.

Keywords: Limestone; Phosphate; Nickel; Sorption; Calcite; Surface water

1. Introduction

Human activities such as farming, mining and manufacturing, which induce continuous increase of salinity and the input of toxic substances in freshwater in many localities worldwide, are the main factors of surface water pollution [1,2]. Introduction of industrial waste and mine waters into natural surface water bodies explains the frequent presence of toxic cations. Heavy metals, such as Pb, Ni, Co, Zn, Cd, Mn, Cr, etc. represent cations that are very toxic to humans, flora and fauna [3–6].

Considering the huge volumes of natural surface water bodies, the reduction of heavy metal concentrations is a very complex issue. Natural materials with sorption properties that are located near polluted water bodies can be used in such cases. Natural sorbents such as zeolites, kaoline, tuffs, limestone are suitable [2,7–11]. Attempts have been made earlier to remove heavy metals using various purification systems, the simplest being the addition of lime and sodium hydroxide. This method can be used to treat mine waters, but not surface waters. Other chemical [12], biological and microbiological [1] methods have also been applied.

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The papers [13–17] present the results of studies that were carried out to test the absorption of divalent cations (Pb^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+}, Co^{2+}, etc.) using limestone. In addition, limestone was used to stabilize heavy metals accumulated in the bottom of a water body [6].

For example, fish from acidified lakes in Sweden often display elevated levels of mercury [18–20]. The use of limestone has led to a decrease in the mercury content in fish by 20%. Decrease in the mercury content was observed in lakes where the liming resulted in pH increase by more than 0.5 units and only when the pH did not exceed 6. Liming to pH levels >6.5 did not give acceptable results. Available data suggest that liming does not always reduce mercury levels in fish. In general, the process of Hg and heavy metals removal from water by limestone requires deeper analysis of the mechanisms of their reduction [21,22].

Modern studies of heavy metals removal from water by natural carbonates have shown the following results. Calcite and aragonite were used to compare the removal of Pb^{2+} from water [15]. The chemical formula of these minerals is $CaCO_3$ and they differ only in the crystal system. The crystal system of calcite is trigonal, while that of aragonite – orthorhombic. The efficiency of Pb^{2+} removal by calcite was higher compared to aragonite. Thus, when using natural limestone for environmental technologies to improve water quality, in addition to the properties of the pollutants, it is necessary to take into account the crystal system [15] and size [23,24].

Numerous papers [13–15,17] have reported that removal of heavy metal cations by limestone takes place through the ion-exchange mechanism or by sorption through the surface. At the contact of limestone with water, through the formation of Ca^{2+} ions in water, the water pH value increases and, as a result, HCO_3^- bicarbonate is converted into CO_3^{2-} carbonate. The vast majority of heavy metal carbonates is insoluble and has a very low solubility coefficient [4,25] (Table 1). The formation of insoluble carbonates proceeds as follows [Eq. (1)]:

$$Me^{2+}_{aq} + CO_3^{2-} = MeCO_3 \downarrow \tag{1}$$

Such metals as Ni^{2+} are readily adsorbed by calcite from unsaturated solutions [17,27,28]. Recrystallization of the surface in the absence of a liquid leads to rearrangement of calcite surfaces exposed to Ni^{2+} solutions. As stated in the work [15], such adsorbed ions as Pb^{2+} and Ni^{2+} can be absorbed by the mineral (calcite) in bulk quantities and the process of their absorption is relatively slow.

The most common anionic pollutants of natural surface waters are PO_4^{3-} and SO_4^{2-}. The source of higher PO_4^{3-} levels is surface runoff from farmlands and communal waste water [29]. This anion is often one of the main factors of surface water eutrophication. It plays the role of a useful nutrient for flora and fauna. Active development of phyto- and zooplankton very often causes recreational aesthetic problems [30–32]. The main source of SO_4^{2-} in surface water is the ingress of drainage mine water [4,24,33,34].

To reduce the concentration of PO_4^{3-}, chemical coagulants such as $Al_2(SO_4)_3$ and $FeCl_3$ are often used [35]. Also, bentonite lanthanum (Phospholok) is used in some countries [29]. The paper [36] presents the results of studies on the removal of that anion by chemically activated limestone with hydrochloric acid (HCl) taken from natural surface waters. Purification of water by limestone with a small amount of HCl allows to increase the concentration of Ca^{2+} in it. Dissolved Ca^{2+} will bind PO_4^{3-} and form insoluble $Ca_3(PO_4)_2$ [37]. Binding of PO_4^{3-} into insoluble forms is explained by the fact that $Ca_3(PO_4)_2$ has a very low solubility coefficient of only 1.3×10^{-32} at 25°C, whereas that of $CaCO_3$ is 8.7×10^{-9} at 25°C. PO_4^{3-} removal by limestone takes place according to the following chemical reactions:

Table 1
Solubility of selected metal carbonates [23,26]

Metal carbonate type	Solubility
$MgCO_3$	3.2×10^{-8}
$CaSO_4$	2.5×10^{-5}
$CaCO_3$ (calcite)	4.5×10^{-9}
$BaCO_3$	5.0×10^{-9}
$MnCO_3$	5.0×10^{-10}
$FeCO_3$	2.0×10^{-11}
$NiCO_3$	1.3×10^{-7}
$ZnCO_3$	1.0×10^{-10}
$PbCO_3$	8.0×10^{-14}

$$CaCO_3 = Ca^{2+} + HCO_3^-\left(CO_3^{2-}\right) \tag{2}$$

$$Ca^{2+} + PO_4^{3-} = Ca_3\left(PO_4\right)_2 \downarrow \tag{3}$$

The essence of SO_4^{2-} removal by limestone from water takes place according to the same chemical reactions as PO_4^{3-} removal (2 and 3) [37,38]. Limestone is widely used for purification of surface water from cationic (heavy metals) and anionic (PO_4^{3-}, SO_4^{2-}) pollutants [4,15,27,36].

Thus, products of limestone dissolution can participate in the process of water purification from cationic and anionic impurities. Heavy metals can be removed from water by precipitation in the form of insoluble carbonates. Anionic pollutants (PO_4^{3-} and SO_4^{2-}) can be removed by the formation of insoluble calcium salts. In addition, some metals (Hg^{2+}, Ni^{2+}) can be adsorbed onto the limestone surfaces. Thus, the recovery of Hg^{2+} and Ni^{2+} must be considered as the adsorption on the limestone (calcite) surface; the strive for equilibrium and the negative charge of calcite causes metals to be adsorbed on its surface.

Using this method, all heavy metals may be removed from water using limestone. The process depends on the formation of insoluble metal carbonates. When heavy metals form insoluble carbonates, then the process should take place in alkaline conditions. In another case, the compounds may be absorbed on the limestone surface. The absorption efficiency depends on the water pH.

Dispersed natural limestone is often used for the purification of surface water. It is a cheap by-product of limestone quarries. Therefore, water purification with application of dispersed limestone is relevant both from environmental and economic points of view. The mineral powder is produced from the by-products of limestone quarries. Production of the mineral powder requires energy; this applies to the technological process, that is, grinding of limestone in mills at high temperatures.

The properties of natural limestone and mineral powder are different. The pH, Eh and total dissolved solids (TDS) increase will be higher after addition of the mineral powder rather than natural limestone to the water. Thus, usage of the mineral powder for water purification will be more expensive than application of natural limestone.

Comparative analysis was made for dispersed, thermally activated limestone and natural limestone from Ternopil Quarry in Ukraine. The study is aimed at analysing and modelling a case when the water contains pollutants, whose removal by limestone is possible through adsorption and formation of insoluble carbonates. We wanted to show the conditions in which the analysed limestones can be used. After addition to water, the change of physical and chemical properties will take place at various speed. This will influence the efficiency and safety of the process.

1.1. Geological situation and characteristics of the limestone

The analysed limestone deposit occurs within the Tovtry Ridge in the Ternopil and Khmelnytsky regions of Ukraine. The Tovtry Ridge is clearly expressed in the landscape and composes a chain of hills with absolute elevations of 400–486 m. Geologically, the Tovtry is a complex of massive Miocene limestones with a thickness of 1.5 to 55 m (Opilsky, Kosovska Mira, Volhyn beds), occurring on the eroded surface of Paleogene or Cretaceous deposits (sands, sandstones, marls). The width of the ridge reaches 15–20 km and its length exceeds 200 km.

Bioclastic carbonate rocks in Western Ukraine cover vast areas. Two large areas represent Cretaceous and Neogene limestones, co-occurring with each other in the Rivne-Ternopil area (Fig. 1). In particular, this may be observed in the Mizotsky Ridge (Zdolbunovskaya quarry) and in the Kremenetsky Medobory hills, where Neogene sands and Sarmatian limestone-shell rocks overlie a thick Cretaceous succession.

According to geological studies, the limestone composition in the region is homogenous. The limestones are dense, recrystallized and characterized by a high calcium content ($CaCO_3$ content exceeding 90%). Recrystallized limestones are characterized by a fairly large bulk density and mechanical strength. In Ukraine, limestones of the Tovtry Ridge are used as raw material for the steel industry as fluxes for rubble stone, the sugar industry, and in lime production. In the process of limestone crushing and fractionating, a significant amount of dispersed waste is formed with a grain size composition of the limestone fragments within 0–20 mm. Such limestone waste is stored in quarry dumps and its volume exceeds 3.5 million tons, with a monthly increase of about 100 thousand tons. A general view of a working limestone quarry with accumulated heaps of limestone waste is presented in Fig. 2.

Such limestone dumps in the form of waste heaps create man-made landscapes and disrupt the natural environmental balance. Therefore, there is an acute problem of their use as secondary raw material for industrial waste. Considering their enormous volume, a promising direction is the use of limestone for the sanitation of natural surface water. The use of limestones is possible provided their properties are first investigated.

2. Methods and material

2.1. Study material

In many quarries, the processing of natural carbonates (limestone) leads to the accumulation of weak rocks, the grain size of which is below 20 mm. It is impossible to obtain from them crushed stone meeting the requirements for solution fillers. Therefore, dispersed limestone is produced from such limestone waste, further used as a mineral fertilizer. The technological process for such

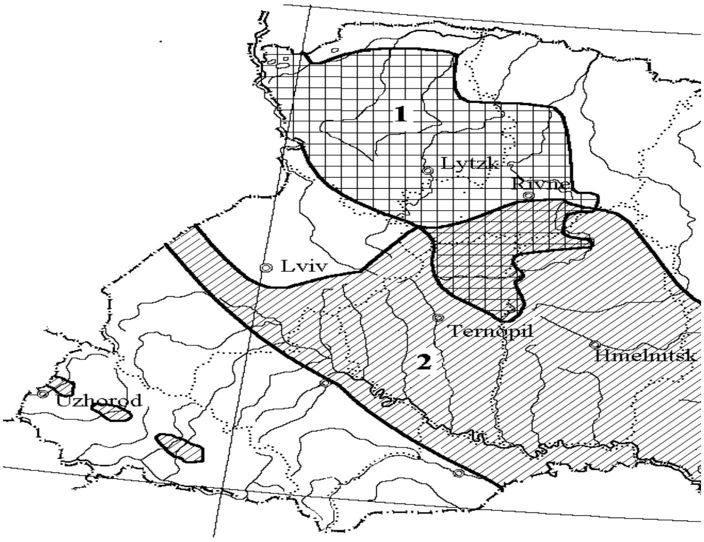

Fig. 1. Areas of distribution of Cretaceous (1) and Neogene limestones (2) in Western Ukraine.

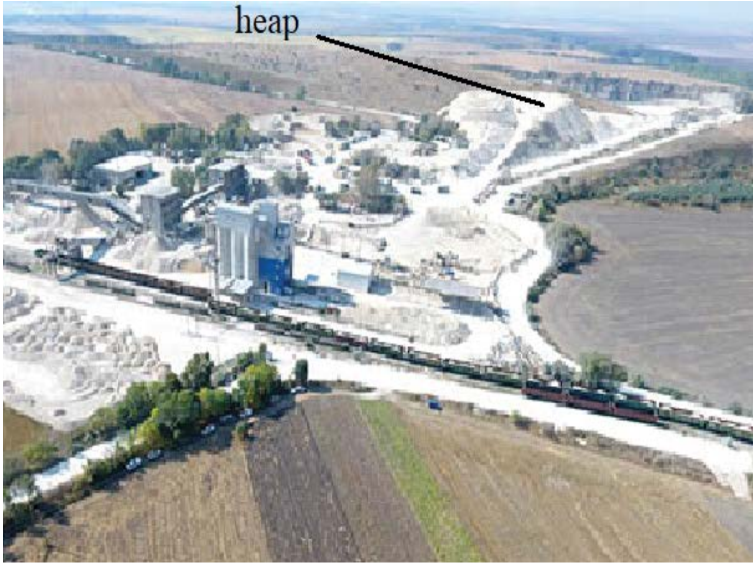

Fig. 2. General view of a working limestone quarry with accumulated heaps of limestone waste.

mineral fertilizer production is as follows: the original limestone is fed to a ball mill, in which it is dispersed; during this process, limestone is simultaneously dried at a temperature of 240°C–250°C.

For the comparison of Ni^{2+} and PO_4^{3-} removal, dispersed, thermally activated calcite (TA-Cal) and natural calcite (N-Cal) were used; in each case, the grain size was below 0.1 mm. The general view of the samples is presented in Fig. 4.

Before the beginning of the experimental studies, samples of the studied limestones were dried at a temperature of 105°C until their mass was stabilized. It was necessary to remove physically bound water from the limestone surface.

2.2. Chemical and mineralogical analysis of the analysed limestones

The chemical composition of the two limestone samples was determined using X-ray fluorescence (XRF). Chemical analyses were performed using X-ray spectral analysis with the ARL Advant'X instrument. Loss on ignition (LOI) was determined by weight loss after roasting the samples at 950°C.

The mineral composition of the TA-Cal and N-Cal samples was determined by powder X-ray diffraction using a Marvel X-ray diffractometer (PANalytical Mineral). In order to precisely determine the amount of the main rock-forming minerals (calcite), the samples were recorded in the range of 6.5°–65°2θ, with 2.1 step/s and step width 0.022°2θ.

2.3. Experimental analysis of Ni^{2+} removal by the analysed limestones

To study Ni^{2+} adsorption by TA-Cal and N-Cal at different doses (2.0 and 4.0 g/L), initial pH of 5 and 7, and TDS of 0.02 and 0.55 g/L, a freshly prepared solution of $NiSO_4$ was used. The concentration of Ni^{2+} was 8.75 mg/L. The studied limestone samples at 0.2 and 0.4 g were placed in a plastic flask. Afterwards, 100 ± 1 mL of the Ni^{2+} solution was added to a beaker. Later, the plastic flacks were stirred at 180 rpm in a shaker. The first series of experimental studies of Ni^{2+} removal from the water solution by the analysed limestones was carried out for 24 h and the second series of studies was performed for 4 d. Each experiment was repeated at least twice. After the specified reaction time, the pH, Eh (which is a measure of the redox state of a solution), and TDS values were measured immediately following each experiment. Later, 50 mL of the solution was filtered using a disposable cellulose filter.

The calculation of the Ni^{2+} adsorfigption capacity was performed according to Eq. (4):

$$q = \frac{\left(C_0 - C_i\right) \cdot V}{m}, \text{ mg/g} \tag{4}$$

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

2.4. Experimental analysis of PO_4^{3-} removal by the analysed limestones

A solution containing 6.5 mg/L of PO_4^{3-} was prepared by dissolving trisodium phosphate $Na_3PO_4 \cdot 12H_2O$ in distilled water. Afterwards, the pH of the initial PO_4^{3-} solution and the TDS were adjusted to a desired value using 0.1 M NaOH or HCl solutions. The test of the efficiency of variable pH and different initial doses of TA-Cal and N-Cal (2.0 and 4.0 g/L) on PO_4^{3-} removal was carried out at the temperature of 15°C for 4 d. Exactly 0.2 and 0.4 g of TA-Cal and N-Cal were mixed with 100 mL of PO_4^{3-} concentration at 6.5 mg/L (pH pre-adjusted to the desired value) in a 150 mL flask.

The mixture was stirred at 180 rpm at the temperature of 15°C in a shaker. After 0.5, 1, 2, 3 and 4 d, the solution was

Fig. 3. (a) Dispersed, thermally activated limestone and (b) natural limestone.

filtered through a cellulose acetate membrane. Each experiment was repeated at least twice. After the specified reaction time, the pH, Eh, and TDS values were determined using a multimeter immediately after each experiment. Each filtrate was analysed for residual PO_4^{3-} concentration. PO_4^{3-} analysis was performed using the molybdenum-blue ascorbic acid method using a UV–vis spectrophotometer (UV/VIS 1600).

3. Results

3.1. Results of XRD and XRF analyses

X-ray fluorescence analyses indicated that the main component of both limestones studied (TA-Cal and N-Cal) was CaO with the contribution of 52.7% and 52.9%, respectively. In addition, limestone loss by ignition attained similar values of 43.2% and 43.1%, respectively.

To characterize the crystal structures of TA-Cal and N-Cal, X-ray diffraction analysis was carried out (in the 2θ range of 5°–65°) (Fig. 4). For TA-Cal and N-Cal, the diffraction peaks at 23.2°, 29.5°, 39.4°, 43.8°, 43.4°, and 50.4° were attributed to calcite, and the peaks at 47.2° and 48.8° to quartz (Fig. 4). There were no additional peaks in the diffractograms of the analysed limestones.

The mineral occurring in the limestone, as indicated by the analysis, is trigonal calcite. Its percentage composition in TA-Sal and N-Cal is 98.6% and 98.7%, respectively. According to the diffractometer determination of the mineral composition of the limestones, they are represented by calcite in terms of mineralogy. Marine benthic reef organisms used this mineral to build their skeletons in two modifications, as tetrahedral and rhombohedral crystal cells. Both these modifications could be syngenetic and correspond to the time of existence of the organisms that built them.

Calcite is a common mineral in Earth's crust [39]. Chemical analyses have shown that it may contain some cations, such as Fe, Mg, Al, and Mn. When calcite precipitates, divalent cations are taken up, depending on whether the calcite is formed in an inorganic or organic process as a result of biological activity, such as in mollusc shells or earthworm excrements [13,28]. Divalent cations with atomic radii equivalent to or smaller than that of calcium, are often substituted with little or no disruption into the atomic structure. Lattice crystals can also tolerate a certain fraction of larger divalent cations.

The obtained results indicate that during the preparation of dispersed, thermally activated limestone there were no changes in either the chemical composition or the structure of the calcite crystals.

3.2. Ni^{2+} removal with TA-Cal and N-Cal samples

Analysing the solubility coefficient of the products (Table 1), that is, K_{SP} of $NiCO_3$ = 1.3×10^{-7} and K_{SP} of $CaCO_3 = 3.8 \times 10^{-9}$, it is obvious that when limestone is added to water, Ni^{2+} cannot precipitate as insoluble $NiCO_3$ (gaspeite). This fact is also confirmed by the results obtained in the paper [17]. Thus, Ni^{2+} removal from water solutions was considered as its adsorption on the surface of limestone (calcite).

For comparative experimental studies of the possibility of Ni^{2+} recovery, TA-Cal and N-Cal samples were taken at doses of 2.0 and 4.0 g/L. The experiments were carried out at initial water pH values of 5 and 7. Such initial water parameters were taken for assessment of Ni^{2+} removal from water solutions with a naturally real pH value of surface water. The initial values of water TDS were 0.02 and 0.55 g/L. Water TDS values of 0.55 g/L were adopted in order to maximize the approximation of the experimental conditions to natural conditions, since the value of water TDS can change during the year and such value often can be the maximum [32,40].

Analysis of the obtained results (Fig. 6) shows that the adsorption capacity of Ni^{2+} depends on the dose of the studied limestones and the level of water pH increase. Thus, the highest adsorption capacity of Ni^{2+} (q = 3.43 mg/g) was observed upon its contact with TA-Cal at a dose of 2.0 g/L.

Simultaneously with the determination of Ni^{2+} adsorption capacity with TA-Cal and N-Cal, changes of pH, Eh, and TDS values were determined. Assessment of the changes in those water parameters was carried out until achieving chemical equilibrium. Such dependencies are shown in Fig. 5a and b.

Fig. 5a and b indicate that changes in pH, Eh, and TDS values depend on the dose of TA-Cal. Thus, at addition of

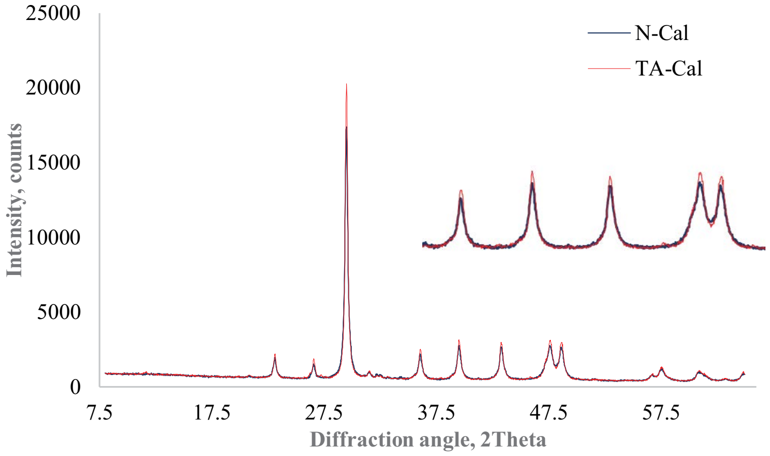

Fig. 4. X-ray patterns of the TA-Cal and N-Cal samples.

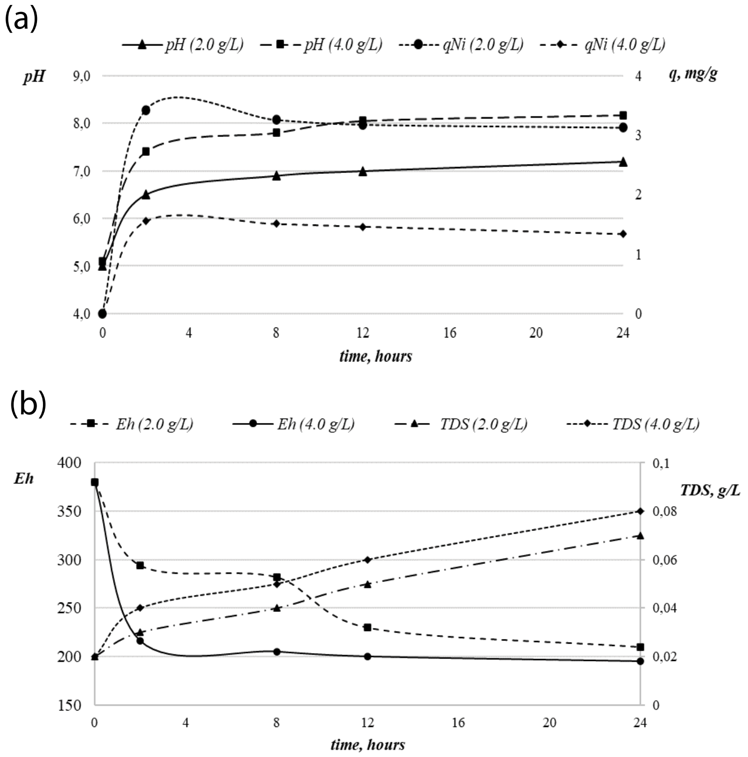

Fig. 5. (a) Change in the Ni^{2+} adsorption capacity and pH values depending on TA-Cal doses (2.0 and 4.0 g/L) until chemical equilibrium. (b) Change in the Eh and TDS values depending on TA-Cal doses (2.0 and 4.0 g/L) until chemical equilibrium.

2.0 g/L of TA-Cal to water, the water pH increased by 2.2, and at addition of 4.0 g/L it increased by 3.2. It should be noted that upon water contact with 2.0 g/L of TA-Cal, the Eh value decreased by 170 mV and upon contact with 4.0 g/L – decreased by 170 mV. An increase in the TDS value was also observed, which depends on the dose of TA-Cal. Similar experimental studies of the dependence of the pH, Eh, and TDS change with the addition of 2.0 and 4.0 g/L TA-Cal and N-Cal, and simultaneous determination of Ni^{2+} adsorption capacity, were carried out at initial pH = 7 and TDS = 0.02 and at 0.55 g/L of water solution.

When N-Cal (with similar initial water parameters) at a dose of 2.0 g/L was added to the water, the Ni^{2+} adsorption capacity was higher than when it was added at a dose of 4.0 g/L, and was q = 1.71 mg/g and q = 0.98 mg/g, respectively (Table 2).

The studies have shown that the Ni^{2+} adsorption capacity at the addition of 2.0 g/L of TA-Cal and N-Cal was higher than at the addition of 4.0 g/L of these limestone samples. Based on this, doses of 2.0 g/L of TA-Cal and N-Cal were taken for the following studies. Experimental studies of Ni^{2+} adsorption were carried out for 4 d (until the establishment of chemical equilibrium) and showed the following. During the 1st day, Ni^{2+} adsorption prevailed over its desorption. In the interval from the 2nd day to the 3rd day, the process of Ni^{2+} desorption was observed during its contact with the two investigated limestone samples. Desorption returned Ni^{2+} to the solution until its concentration on the calcite solid became high enough for the desorption and adsorption rates to become equal. This equilibrium state was observed from the 3rd to the 4th day of the observations. Similar studies and results were also obtained and presented in the papers (Andersson et al. [13]; Hoffmann and Stipp [17]). Changes in Ni^{2+} concentration and pH, Eh, and TDS values (at initial TDS of water at 0.02 and 0.55 g/L, pH = 5 and 7) are presented in Fig. 6a and b.

As observed in Fig. 6a and b, one day after the experiment started, Ni^{2+} adsorption capacity by TA-Cal was 3.45 mg/g (at TDS 0.02.0 g/L) and 2.03 mg/g (at TDS 0.55 g/L). On the 2nd day of the observations, Ni^{2+} adsorption capacity decreased in comparison to the 1st day. Increase of water pH (initial TDS = 0.02 and 0.55 g/L) was observed for 4 d and the chemical equilibrium occurred on the 4th day when pH = 8.2.

During the 2nd, 3rd, and 4th days, an increase in the pH, Eh and TDS values occurred. It was not as fast as during the 1st day of the experiment. On the 1st day (at initial pH = 5, TDS = 0.02 g/L), ΔpH = 2, ΔEh = –90 mV, and ΔTDS = 0.05 g/L. Changes in these parameters (initial pH = 5, TDS = 0.55 g/L) were as follows: ΔpH = 1.11, ΔEh = –50 mV, and ΔTDS = 0.14 g/L.

3.4. PO_4^{3-} *removal by TA-Cal and N-Cal samples*

The effect of PO_4^{3-} sedimentation in the form of $Ca_3(PO_4)_2$ depends on the concentration of calcium. When limestone is added to water, the formation of insoluble calcium PO_4^{3-} occurs through a significant difference in solubility products, that is, the solubility coefficient K_{SP} of $CaCO_3 = 3.8 \times 10^{-9}$ is less than the K_{SP} of $Ca_3(PO_4)_2 = 2.0 \times 10^{-29}$ [26].

For experimental studies, the initial pH and TDS values were the same as in the analysis of Ni^{2+} removal by TA-Cal and N-Cal. Experimental studies were carried out for 4 d, that is, before achieving the chemical equilibrium for all controlled parameters. The obtained results of PO_4^{3-} removal by TA-Cal from the water solution and changes of the water quality parameters are shown in Fig. 5. Fig. 5a and b shows that the levels of PO_4^{3-} removal and pH, Eh and TDS change depended on the dose of TA-Cal. Experimental studies were carried out until chemical equilibrium was achieved by all four water indicators. The chemical equilibrium of pH was reached in 1 d, but for PO_4^{3-}, Eh and TDS the equilibrium was reached after 3 d. When adding a dose of 2.0 g/L of TA-Cal, the maximum pH value of water was 7.9, and of 4.0 g/L – 8.3.

The trend of the TDS value was different over the course of 4 d. From the moment of limestone contact with a water solution and during the 1st day, the TDS value increased. At this time, it saturated with Ca^{2+} ions in the water solution. At the same time insoluble $Ca_3(PO_4)_2$ was formed when the water solution was saturated with Ca^{2+} ions. This was evidenced by the fact that the PO_4^{3-} concentration decreased. The efficiency of PO_4^{3-} removal by a dose of 2.0 g/L was 56.4%, and by a dose of 4.0 g/L – 75.4%.

As indicated in Fig. 8, the Eh value of water was reduced with addition of limestone. The largest decrease of this parameter occurred during the 1st day of the experiment. Decrease of the Eh value of water by adding a dose of 2.0 g/L was 206 mV, and a dose of 4.0 g/L – 233 mV. On the 2nd and further days of the experiment, decrease in the Eh of water was insignificant and practically did not depend on the dose of limestone.

Table 2
Dependence of the change in the pH, Eh and TDS values of water on its initial values and Ni^{2+} adsorption capacity during chemical equilibrium

Limestone	pH	Dose, g/L	TDS, g/L	ΔpH	ΔEh	ΔTDS	*q*, mg/g
TA-Cal	5.0	2.0	0.02	2.2	170	0.05	3.43
TA-Cal	5.0	4.0	0.02	3.2	185	0.06	2.65
N-Cal	5.0	2.0	0.02	1.7	150	0.03	1.73
N-Cal	5.0	4.0	0.02	2.2	160	0.04	1.58
TA-Cal	7.0	2.0	0.02	1.5	140	0.03	1.59
TA-Cal	7.0	4.0	0.02	2.1	155	0.04	0.78
N-Cal	7.0	2.0	0.02	1.2	123	0.02	0.82
N-Cal	7.0	4.0	0.02	1.6	106	0.04	0.73
TA-Cal	5.0	2.0	0.55	1.8	121	0.03	2.89
TA-Cal	5.0	4.0	0.55	2.6	129	0.05	0.88
N-Cal	5.0	2.0	0.55	1.3	98	0.02	1.61
N-Cal	5.0	4.0	0.55	1.9	102	0.03	0.76
TA-Cal	7.0	2.0	0.55	1.3	95	0.02	0.86
TA-Cal	7.0	4.0	0.55	1.6	99	0.04	
N-Cal	7.0	2.0	0.55	1.1	86	0.02	0.78
N-Cal	7.0	4.0	0.55	1.4	83	0.03	0.63

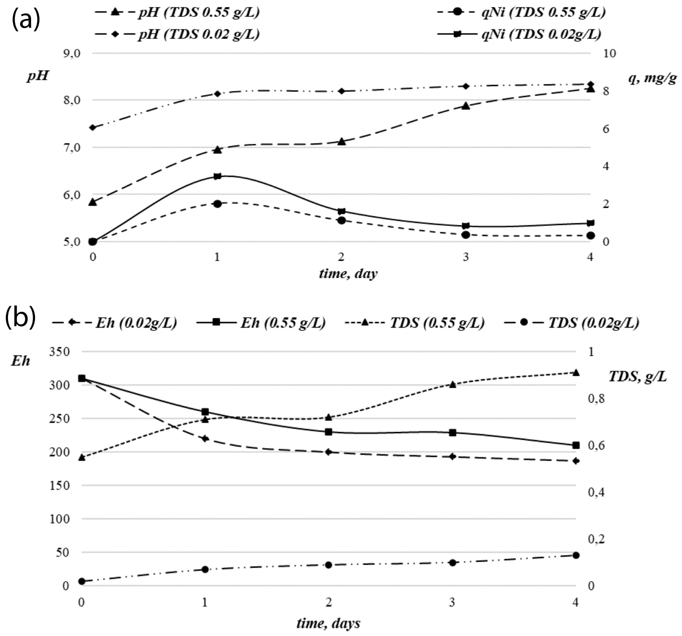

Fig. 6. (a) Dependence of the change in the values of Ni^{2+} adsorption capacity and pH (at initial TDS = 0.02 and 0.55 g/L) on the added TA-Cal sample at chemical equilibrium. (b) Dependence of the change in the Eh and TDS values (at initial TDS = 0.02 and 0.55 g/L) on the added TA-Cal sample at chemical equilibrium.

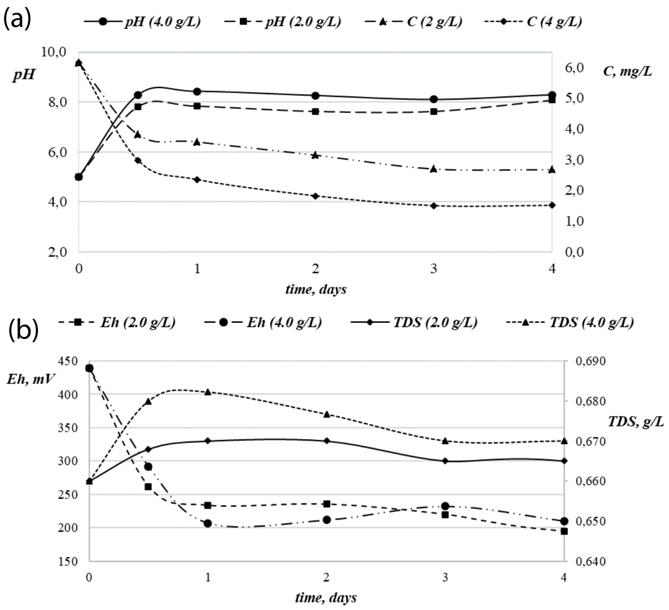

Fig. 7. (a) Dependency of the changes of PO_4^{3-} concentration and water pH after adding 2.0 and 4.0 g/L of TA-Cal doses. (b) Dependency of the changes of Eh and TDS of water after adding 2.0 and 4.0 g/L of TA-Cal doses.

The same algorithm was applied for experimental studies using N-Cal at doses 2.0 and 4.0 g/L, pH 5 and 7, TDS 0.02 and 0.55 g/L. The results are presented in Table 3. With increase in the initial water pH, the rate of limestone dissolution and the efficiency of PO_4^{3-} removal from water by the analysed limestones decreased. As shown in Table 3, when TA-Cal and N-Cal samples at a dose of 2.0 g/L are added to water with the same initial parameters, the removal efficiency was lower in comparison with the dose of 4 g/L. The efficiency of PO_4^{3-} removal in the case of the dose of 2.0 g/L TA-Cal was about 10%–15% higher than when N-Cal was added. The water Eh changes, as indicated by the studies, depend on the initial pH value, the TDS of water, and the doses of TA-Cal and N-Cal. At doses of 2.0 and 4.0 g/L, TDS 0.55 g/L, pH 5 and 7, there was no significant difference between the reduced values of this water parameter.

With PO_4^{3-} removal by limestone, a decrease in water TDS was observed. Similar trends in the change of water TDS during the removal of anionic pollutants by the addition of natural carbonate are presented in the paper [41].

When changes in the TDS value during Ni^{2+} and PO_4^{3-} removal were compared, a significant difference was observed. Namely, when Ni^{2+} was removed from water, the TDS value always increased over the course of 4 d. When PO_4^{3-} was removed, the value of this parameter increased during the 1st day, but later decreased. This is due to the fact that the removal of cationic and anionic pollutants by limestone occurs according to different mechanisms.

4. Discussion

Comparative experimental studies have shown that TA-Cal and N-Cal samples are capable of Ni^{2+} and PO_4^{3-} removal from water solutions. TA-Cal is shown to be more efficient in removing such contaminants from water solutions. This can be explained as follows. XRD analyses of these limestones showed that their main mineral is trigonal calcite. Its percentage is 98% and the structure of the calcite crystal at temperatures in the range of 240°C–250°C was not disturbed. Under the influence of temperature difference as a result of spatial anisotropy of thermal conductivity and increase in the expansion coefficient of the crystals, a large number of points of internal stresses arise in the calcite crystals. This process leads to cracking (decrepitation) of calcite crystals along cleavage planes oriented in three directions within the rhombohedron [42,43]. As a result of thermal decrepitation of calcite, crystallization water and gas inclusions are released from the crystal. Moreover, there is a relationship between the particle size of limestone and its tendency to decrepitate [44]. Limestone particles less than 1 mm in size show an increased tendency towards decrepitation. For limestone, the most critical dimensions are in the range of 150–1180 mm, in particular in the range of 425–850 mm. Therefore, limestone preliminarily crushed to a dispersed state is more exposed to decrepitation and cracking of calcite crystals.

As a result, the decrepitation of calcite leads to increased activity of limestone in water. Namely, it dissolves faster that crushed natural limestone. As a result, upon contact with water, limestone dissociates at a higher speed into Ca^{2+} and CO_3^{2-} ions. The increase of pH and TDS values of water is also faster. The surface of such calcite crystal quickly acquires excess negative charge. Thus, heavy metals can be more rapidly attracted to the negatively charged limestone crystal.

Our studies have shown that TA-Cal and N-Cal samples are capable of Ni^{2+} and PO_4^{3-} removal from water. Moreover, we have proved experimentally that the efficiency of these processes depends on the rate of the water pH value increase. Results of the experimental studies have shown that (at initial values of pH = 5 and 7, TDS = 0.02 and 0.55 g/L) after adding doses of 2.0 g/L of TA-Cal and N-Cal, the Ni^{2+} adsorption capacity was always higher than after adding doses of 4 g/L. The value of Ni^{2+} sorption capacity was higher when using TA-Cal. The efficiency of PO_4^{3-} removal was higher when using TA-Cal at a dose of 4.0 g/L than at the same dose of N-Cal. The explanation for this is that as the dose of limestone increased, the rate of change in water pH also increased. As commonly known, the calcite crystal can be negatively charged in water. At increased water pH, the value of the calcite negative charge decreases. Therefore, electrostatic repulsion rises between Ni^{2+} ions and the calcite crystal, causing decrease of the adsorption capacity. Similar results of the dependence of the adsorption capacity of heavy metals on the dose of the natural adsorbent were obtained in the papers [3,10,45].

With a rapid increase in water pH, the process of Ni^{2+} desorption can be equated with adsorption. Therefore, if it is necessary to remove heavy metals that either do not form insoluble carbonates (for example, Hg) [23], or the value of the solubility product is smaller than the value of this

Table 3
Results of changes in water parameters and PO_4^{3-} concentration at application of different doses of TA-Cal and N-Cal

Limestone	pH	Dose, g/L	TDS, g/L	ΔpH	ΔEh	ΔTDS	C, mg/L
TA-Cal	5.0	2.0	0.02	2.84	244	0.005	2.68
TA-Cal	5.0	4.0	0.02	3.4	229	0.01	1.51
N-Cal	5.0	2.0	0.02	2.02	195	0.005	2.97
N-Cal	5.0	4.0	0.02	2.85	176	0.01	1.96
TA-Cal	7.0	2.0	0.02	1.71	204	0.005	2.89
TA-Cal	7.0	4.0	0.02	2.41	198	0.01	1.78
N-Cal	7.0	2.0	0.02	1.45	173	0.005	3.86
N-Cal	7.0	4.0	0.02	1.59	164	0.01	3.04
TA-Cal	5.0	2.0	0.55	2.56	168	0.005	2.03
TA-Cal	5.0	4.0	0.55	2.77	170	0.01	1.24
N-Cal	5.0	2.0	0.55	1.91	156	0.005	2.04
N-Cal	5.0	4.0	0.55	2.06	162	0.005	1.52
TA-Cal	7.0	2.0	0.55	1.25	136	0.005	2.31
TA-Cal	7.0	4.0	0.55	1.61	129	0.005	1.43
N-Cal	7.0	2.0	0.55	1.05	106	0.005	3.10
N-Cal	7.0	4.0	0.55	1.13	98	0.005	2.46

coefficient of $CaCO_3$ (for example, Ni^{2+}), the general factor in ensuring the process efficiency is water pH increase [18].

In this case, it is more practical to use natural limestone. Samples of this material have bigger sizes of the mineral aggregate than in the case of dispersed, thermally activated limestone, therefore they will dissolve more slowly and retain heavy metals for a long time [46,47].

To obtain such results and then introduce them into practice, it is very important follow the recommendations of the EPA (Environmental Protection Agency) [16,21,48]. As commonly known, adding limestone to natural waters is a well-known practice that has been applied for a long time. However, the main condition for using this natural material is that when it is added for the first time, the water pH should not exceed 1.5. Otherwise, living organisms (flora and fauna) can get chemical burns [49]. Guided by the recommendations of the EPA [46,48], namely those for the safe addition of limestone, its application for purification of surface waters can be made according to the following algorithm. Because the solubility rate of TA-Cal is higher than that of N-Cal, it will be more efficient of removal PO_4^{3-} from water. When adding TA-Cal to water, the increase in water pH should be controlled. TA-Cal must be introduced into water in as uniform state as possible on the surface of the water body. To obtain the desired effect, adding such limestone is possible several times during a certain interval.

Moreover, experimental studies of Ni^{2+} and PO_4^{3-} removal from water solutions have shown that, regardless of the initial water parameters (pH, TDS), addition of limestone at different doses always cause decrease in the water Eh value. As presented in the article [50], decrease in the Eh value of natural waters with the addition of limestone will help to reduce the development of pathogenic bacteria and improve the state of the surface water as a whole.

Pegler et al. [51] postulates that during liming of natural waters, the greatest change was observed after liming of watersheds. This impact was related to changes in the quality of bottom sediments, food quality and zoobenthos habitats. This is crucial for a better understanding of the impact of pollution and recovery of biotic communities, important for determining the overall recovery effectiveness and setting appropriate management objectives for the liming process of surface waters.

Currently, there are numerous arguments that speak against liming, based on the assumption that during such process alters the ecosystem natural disturbance regime [52,53]. Very often, the presence of heavy metals in natural surface waters is the result of anthropogenic influence. There are cases when such water bodies are the only source of water supply for human settlements. Furthermore, when deciding on the use of limestone, it is necessary to carefully assess the possible risks of mass human illnesses, since traditional water treatment plants are not able to extract various heavy metals from water [54].

5. Conclusions

Experimental studies have indicated that the extraction effectiveness of cationic and anionic pollutants (e.g., Ni^{2+} and PO_4^{3-}) from the analysed water solutions is higher at application of dispersed, thermally activated limestone. The effectiveness of the removal of these pollutants strictly depends on the rate of water pH increase. The obtained results are of significant practical value. Selection of the limestone type requires assessment of its negative impact on the environment, because limestone application must be safe for the flora and fauna. Liming of natural water bodies should follow the recommendations of the EPA (Environmental Protection Agency), that is, at first application of limestone the water pH should not exceed 1.5.

Moreover, it should be emphasised that if the water body is the source of water supply for human settlements and the existing pollutants may be removed by limestone by its deposition in a slightly alkaline setting, then it is recommended to use dispersed, thermally activated limestone. If the water contains heavy metals, whose removal is possible through the adsorption mechanism, then it is recommended to apply natural crushed limestone to decrease the heavy metal content. This results from the slow increase of water pH and in consequence – from slow desorption.

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