UDC 544.77
DOI: 10.15587/1729-4061.2024.298913

PHYSICO-CHEMICAL STUDY OF THE ADSORPTION PROPERTIES OF NATURAL MINERALS FOR SORPTION TREATMENT OF WASTEWATER FROM PB^{+2}, NI^{+2}, ZN^{+2} IONS

Manshuk Murzagaliyeva
Candidate of Chemical Sciences, Associate Professor*
Nazgul Ashimkhan
Corresponding author
Candidate of Chemical Sciences, Associate Professor*
E-mail: nazgul.ashimkhan@mail.ru
Ardak Sapiyeva
Candidate of Chemical Sciences, Associate Professor
Department of General and Biological Chemistry
Astana Medical University
Beibitshilik str., 49a, Astana, Republic of Kazakhstan, 010000
Gulnur Daribayeva
PhD
Research Institute of Food Safety
Almaty Technological University
Raimbek str., 348/4, Almaty, Republic of Kazakhstan, 050061
*Department of Chemistry
Asfendiyarov Kazakh National Medical University
Bogenbai str., 151, Almaty, Republic of Kazakhstan, 050000

One of the urgent challenges is to clean up industrial wastewater from toxic and heavy metal ions in a more efficient and environmentally friendly way.

Bentonite montmorillonite, bentonite red, zeolite and diatomite of the Almaty region were selected as the materials of the study.

In this study was investigated the adsorption properties of natural minerals by physico-chemical methods for the sorption treatment of wastewater from Pb^{+2}, Ni^{+2}, Zn^{+2} ions.

X-ray phase analysis determines the chemical composition of the materials studied. The main component of diatomite is SiO_2, in zeolite – Laumontite composition $Ca_4Al_8Si_{16}O_{48}\cdot14H_2O$ (51.3 %). The base of bentonites is bedellite – montmorillonite, which has an amorphous structure. The method of atomic absorption spectrometry was used to investigate the sorption of heavy metal ions (Pb^{+2}, Ni^{+2}, Zn^{+2}) by the natural adsorbents under investigation. Bentonites, Mukra and Medium Tentec have the best sorption properties. Here, the content of lead, nickel and zinc ions is reduced by an average of 82–85 %. In the case of diatomite, the ion content of the same metals is reduced by approximately 74–76 %, and for zeolite by 64 %. Generally speaking, the adsorption properties of these minerals are expected to be achieved by the high porosity in the case of diatomite and zeolite or the penetration of ions into the interpackage space between the bentonite layers. Mixing adsorbents, increasing their mass percentages and increasing the mass of the mixture leads to increased efficiency of the degree of cleaning from these ions.

In conclusion of the study, natural minerals of the Almaty region have sorption properties that can be used for practical purposes, in particular for wastewater treatment

Keywords: water, adsorbent, metal, bentonite, diatomite, sorption, purification, minerals, extraction, kinetics

Received date 23.11.2023
Accepted date 12.02.2024
Published date 28.02.2024

How to Cite: *Murzagaliyeva, M., Ashimkhan, N., Sapiyeva, A., Daribayeva, G. (2024). Physico-chemical study of the adsorption properties of natural minerals for sorption treatment of wastewater from Pb^{+2}, Ni^{+2}, Zn^{+2} ions. Eastern-European Journal of Enterprise Technologies, 1 (10 (127)), 27–35. doi: https://doi.org/10.15587/1729-4061.2024.298913*

1. Introduction

With the development of the industrial sector, the issue of industrial wastewater treatment and waste disposal is increasingly raised. The environmental situation is deteriorating, forcing firms to tighten their requirements for disposal of waste and sewage. It is important to find new approaches to the treatment of wastewater containing metals. Heavy metal ions are the main pollutants in industrial wastewater. The substantial use of heavy metal ions in production leads to their accumulation in the environment and poses a danger [1, 2]. As it is known, almost no enterprise can operate without waste and sewage. When designing production a few years ago, the formation of wastewater, their further recycling and treatment were not taken into consideration. As a rule, it was solved in an increasingly simple way, the sewage was drawn to the nearest point of reception or to the relief (waterway). The effects of the discharge of wastewater were not calculated.

To date, the situation with the discharge of wastewater is changing. The search for and development of the most effective solutions in the field of industrial wastewater treatment is required.

With the emergence of modern wastewater treatment methods, the problems of sewage treatment have begun to find their solutions [3, 4]. The diversity of the composition of sewage determines the breadth of choice of different technological schemes and equipment for their treatment. The range of industrial wastewater treatment equipment includes equipment from different industries, adapted to the required requirements. The existing range of wastewater treatment equipment is constantly expanding with the emergence of new, more efficient technologies.

The main type of galvanic waste is washing water containing a large amount of heavy metal ions [5]. An analysis of existing methods of treatment of natural and heavy metals wastewater has shown that one of the promising is the sorption method using natural inorganic materials as sorbents [6–8].

Therefore, the physico-chemical research of the adsorption properties of natural minerals for the sorption treatment of wastewater from heavy metal ions is relevant.

2. Literature review and problem statement

The authors of the work [9] studied the characteristics of processes of treatment of water from oil and petroleum products with oil sorbents, filtering materials and activated coals. The adsorption capacity of activated coals is due to their developed surface and high porosity. However, the effective extraction of dissolved organic compounds by the sorbent is only possible if the parameters of its porous structure correspond to the size of the molecules of the extracted impurities. The average molecular size of petroleum products is 1.8 nm, so the use of microporous types of activated charcoal to remove these contaminants from the water is often not sufficiently effective because of the spherical inaccessibility for them micropores.

The authors of the work [10] studies showed that of all the filtering materials tested – PPU, STGN, AAA, peat and AU – the most effective on oil products retention are PPUs, STRGNs and activated coal. The disadvantage is the difficulty of fixing the material in the filter, there is no possibility of its regeneration. Thus, for the deep treatment of ship oil-containing waters after their preliminary mechanical (or chemical) treatment for the first phase of sorption, it is recommended to load from PPU and activated charcoal.

On the other hand, activated carbon is widely recognized as the primary adsorbent for various adsorption processes due to its remarkable properties such as large surface area and excellent adsorbing ability. However, it is a relatively high cost and the need for periodic regeneration creates certain problems. This has prompted the search for alternative adsorbents that are readily available and cost-effective. As a result, research is actively looking for new adsorbents to replace activated charcoal.

The authors of the work [11] used sorbents from secondary raw materials to extract heavy metal ions from wastewater. A comparative characteristic of cellulose-containing sorbents compared to activated carbon and cation exchange resins is given. The processing of cellulose-containing materials for the production of sorbents from them is quite expensive, and the cost of the resulting sorbents is close to the price of activated charcoal, although inferior to them in efficiency and absorption capacity. Usually these sorbents are not subject to regeneration.

The authors of the work [12] justifies the possibility of using modified sorbent Akdolit Kesselburger Pelm Gran CM3 (Akdolit-Gran) to neutralize wastewater containing ions of heavy metals Cu (II), Ni (II) and Zn (II), gives a summary characterization of the proposed Sorbent, physico-chemical and sorption properties, determines the mineralogical composition of the sorbent on the basis of data of X-ray structural and thermogrammetric analysis. Akdolit-Gran is an alkaline material prepared from selected dolomite breeds and has undergone thermal modification. This sorbent is produced in Germany. All described methods are developed using foreign raw materials and expensive modifying reagents, many of which are difficult to implement.

The authors of the work [13] considered variants of modification of natural aluminum silicate and carbon mineral raw materials of Kazakhstan. For the study, the ceolite from the previously unexplored field of Kusmurun and the shungite of the Coxa field were selected. It is proposed to modify natural sorbents with a mixture of Tributylphostate and di-2-ethylhexylphosphoric acid in kerosene, phosphorous acid and polyacrylamide mixture, a technogenic raw material. It has been found that when treating both zeolite and shungite with a mixture of phosphoric acid and acid and polyacrylamide, the mechanical strength of the sample is increased, and the mixtion of extractors (di-2-ethylhexylphosphate and Tributylphosphatate) in kerosene contributes to the decrease of its value. The possibility of using technogenic raw materials – phosphorus salts – as modifiers of natural minerals has been demonstrated. However, the labor-intensive modification process is a deterrent to the widespread use of sorbents obtained by this method. Thus, the disadvantages of the described methods are the complexity of implementation, the high cost and the use of deficient reagents.

Natural and synthetic zeolites have found application for the adsorption of organic and inorganic compounds in aquatic environments due to their special physico-chemical properties and the cheapness of the process. The authors of the work [14] presented various parameters for studying the mechanisms of adsorption of organic and inorganic pollutants using zeolites. The main adsorption processes using zeolites as adsorbents include chelation, surface adsorption, natural processes, diffusion, electrostatic interaction and complex formation. It is an excellent adsorbent due to its large area, various surface functions and porosity. Nevertheless, the disadvantage of zeolite is its high cost of preparation and regeneration and, as a consequence, its limited adsorption capacity. However, the latest scientific literature shows that zeolites have been very effective in the treatment of liquid sewage [15].

The authors of the work [16] studied sorbents obtained on the basis of montmorillonite and waste mining enrichment combinate, for adsorption treatment of wastewater from zinc ions. The adsorption properties of manufactured modified sorbents on contaminated wastewater with zinc ions under different conditions were studied. In order to be used as sorbents, clay must be activated by chemical and thermal means to increase and regulate the porosity of their structure, change the chemical nature of the surface.

3. The aim and objectives of the study

The aim of the scientific work is to identifying the adsorption properties of natural minerals by physico-chemical methods for the sorption treatment of wastewater from Pb^{+2}, Ni^{+2}, Zn^{+2} ions.

To achieve this aim, the following objectives are accomplished:

– to study the chemical composition and structure of natural adsorbents by X-ray phase analysis;

– to use an atomic absorption spectrometer to conduct analyses for the content of heavy metal ions in wastewater before and after their treatment;

– to study the kinetics of metallic ions sorption by absorbent mixtures.

4. Methods and materials

The object of the study is environmentally sound technologies.

The hypothesis of the study is possibility of treatment of galvanic plant wastewater containing ions Pb^{+2}, Ni^{+2}, Zn^{+2} with natural sorbents.

The materials of this research are the waste water of the accumulator plant of «Kynar AKB», natural sorbents: diatomite (Ilyan), zeolite (Mytobe), bentonite-montmorillonite (Tentek) and red bentonites (Mukra).

The accepted assumptions include the use of a chemically resistant sorption material that allows for a high concentration of sulfuric acid (pH=1).

The adopted simplifications involve the use of modeling solutions modeling the composition of sulphate-containing washing waters of galvanic production.

Atomic absorption spectrometry. For the analysis of the content of heavy metal ions in wastewater before and after their treatment, the atomic absorption spectrometer MGA-915MD was used.

The principle of operation of the spectrometer is based on the use of the method of Zeeman polarization spectroscopy with high-frequency modulation, which is one of the options of selective atomic-absorption analysis.

The basis of the method used is that the atomizer is placed in a transverse magnetic field with a voltage of about 7.5 kE. Modulated at a frequency of 50 kHz by polarization radiation from the resonance source installed in the working position of the revolver, gets into the atomizer, where the horizontal component of polarization (parallel to the lines of the magnetic field) is absorbed by the identifiable atoms, interfering molecules and aerosols, and the vertical (perpendicular to the magnetic field lines) – only the molecule and the aerosol, i. e. atomic absorption for it is practically absent. At the same time, non-selective absorption for both polarizations is the same. The result is a differential signal with a frequency of 50 kHz, proportional to the concentration of atoms.

Limit of the relative average square deviation of the output signal of the spectrometer at the input of the control solution 6 %.

X-ray phase analysis. The X-rays of the samples were obtained on the diffractometer DRON-3 in digital form using copper radiation. The sampling modes are as follows: voltage on the X-ray tube 30 kV, pipe current 30 mA, movement step of the goniometer 0.05° 2θ and intensity measurement time at the point – 1.0 sec. During the shooting, the specimen was rotating in its own plane at a speed of 60 rpm.

Preliminary X-ray processing to determine the angle position and intensity of reflexes was carried out by the Fpeak program. The analysis was carried out using the PCPDFWIN program with the PDF-2 diffractometric database.

Objects of investigation. Diatomite is a white-grey powder. Diatomite of Ili field. Diatomite density is 1.4 g/cm^3. Bentonite red is a clay of brown or red color. Mukry field. Density is 0.03 g/cm^3. Bentonite montmorillonite – clay, dark gray colour, in touch resembling soap. Middle Tentek field. Density is 1.8 g/cm^3.Ceolite is a dark brown powder. The Maitobe field. Density: 1.9 g/cm^3.

5. Results of physico-chemical methods for studying wastewater treatment using natural adsorbents

5. 1. Results of X-ray analysis of natural adsorbents

Research on the treatment of wastewater from heavy metal ions requires knowledge of the chemical composition and structure of the potential adsorbents used. For this purpose, X-ray phase analysis was carried out on the data of the minerals, which visually demonstrates the qualitative and semi-quantitative composition of the tested minerals [17–19].

Fig. 1 shows a X-ray of the diatomite (Ili field). Preliminary X-ray processing to determine the angle position and intensity of reflexes was carried out by the Fpeak program. The analysis was carried out using the PCPDFWIN program with the PDF-2 diffractometric database.

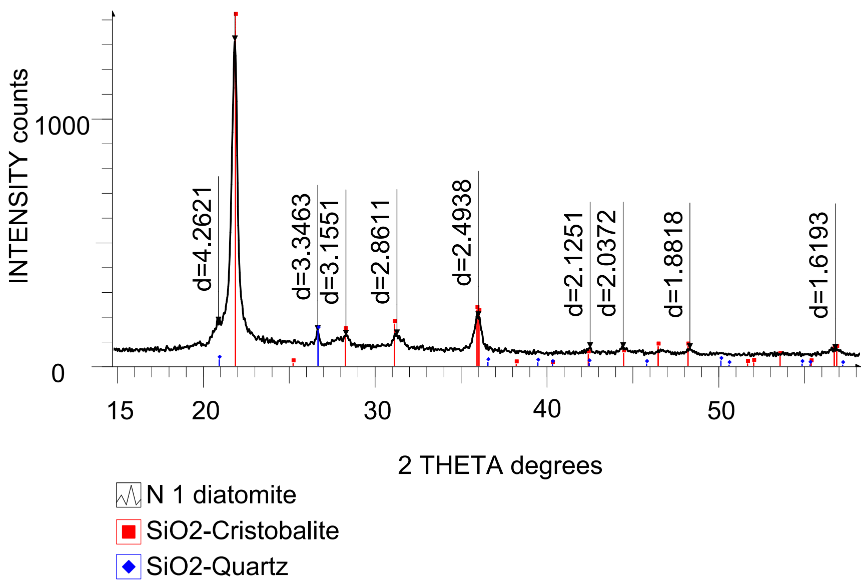

Fig. 1. Diatomite X-ray (Ili field)

On the basis of X-ray, a semi-quantitative analysis of this mineral was made, the data of which are given in Table 1.

Table 1

Results of semi-quantitative analysis of diatomite (Ili field))

Formula	%
SiO_2-Cristobalite	95.7
SiO_2-Quartz	4.3

The diatomite under investigation is silicon oxide, which is present in various forms. Cristobalite is a high-temperature modification of SiO_2 quartz. Cristobalite occurs in the form of spherolites or grapes (balls up to 1 mm in size) in obsidian (volcanic glass), as well as in voids. Sometimes with grown plates of tridimite on crystals of crystobalite, in grain clusters of correct octahedra, rarely in the form of complex cellular structure, pseudo-cubic crystals (spherical crystals), massive forms. It usually has a color ranging from milky-white to yellowish and light brown. It has a high hardness of 6–7, a specific weight of 2.32–2.36 g/cm^3.

Thus, high mechanical hardness, resistance to the action of high temperature, as well as aggressive environments of diatomite is ensured by its composition. The adsorption properties of diatomite are mainly due to its high porosity.

X-ray (Fig. 2) and Table 2 show the main composition of the ceolite (Maitobe field).

As can be seen from the X-rays and the table, cam ceolite is a rather complex mixture of natural minerals, which have their own characteristics and composition. For example, lamontite belongs to the group of zeolites based on aqueous calcium aluminosilicate. It has a hardness on the Moose scale of 3.5–4, with a density of 2.23–2.41 g/cm^3, while it is quite fragile. Heylandite is a mineral, a frame silicate from the group of zeolites. Albite (lat. albus – white) is one of the most common species-forming minerals, white sodium field spat of magmatic origin of the silicate class, aluminosilicate of the plagioclasic group. Augustine (from the Greek αὐγή – “shining, shine”) is a species-forming mineral from the clino-pyroxene group Ca(Mg,Fe,Al)[(Si,Al)$_2$O$_6$]. Coloring from green to black. Hardness 5–6.5. It is part of andesite, basalt, diabasis and other erupted mountain species of predominantly basic nature. Hematite is a common iron mineral, Fe_2O_3, one of the main iron ore. Synonyms: red iron, iron gloss (star.) has a hardness of 5.5–6.5. It’s fragile. Density 4.9–5.3. Vermiculite is a mineral from the group of hydrohumans, having a layered structure, hardness on a mineralogical scale of 1–1.5, density of 2.4–2.7 g/cm^3 (0.065–0.130 g/cm^3).

Vermiculite is biologically stable – is not susceptible to degradation and rotation under the action of microorganisms, is not a favourable environment for insects and rodents, and is chemically inert – neutral to the effects of alkalins and acids. In general, it can be seen that zeolite (Maitobe field) mainly contains minerals, which have a fairly high hardness and mechanical strength. An important property of zeolites is the ability to ionic exchange, due to its crystalline structure, which is formed by the tetrahedrical groups $SiO_{2/4}$ and $AlO_{2/4}$, joined by common peaks into a three-dimensional frame, permeated by cavities and channels (winders) of the size 2–15 angstrom [20, 21].

A similar X-ray analysis was performed with two bentonites. The first bentonite-montmorillonite X-ray is shown in Fig. 3. For this sample, semi-quantitative analysis is virtually impossible due to its low crystallization. Bentonite refers to layered clay, therefore in its structure there are no pronounced crystals, i.e. it is an amorphous material.

In general, the main component of the tested bentonite is bedellite or otherwise – montmorillonite. It is a clay mineral belonging to the subclass of layered silicates. This mineral has a strong ability to swell due to its structure and has pronounced sorption properties.

Table 2

Results of semi-quantitative analysis of zeolite (Maitobe field)

Formula	%
$Ca_4Al_8Si_{16}O_{48}\cdot 14H_2O$ – Laumontite	51.3
$Ca(Si_7Al_2)O_{18}\cdot 6H_2O$ – Heulandite-Ca	16.1
$(Na,Ca)Al(Si,Al)_3O_8$ – Albite	10.1
$N(CaO\cdot(Mg,Fe)O\cdot 2SiO_2)\cdot(Al,Fe)_2O_3$ – Augite	7.6
SiO_2 – Quartz	6.6
$CaCO_3$ – Calcite	6.2
Fe_2O_3 – Haematite	1.9
$Mg_3Si_4O_{10}(OH)_2$ – Vermiculite	0.2

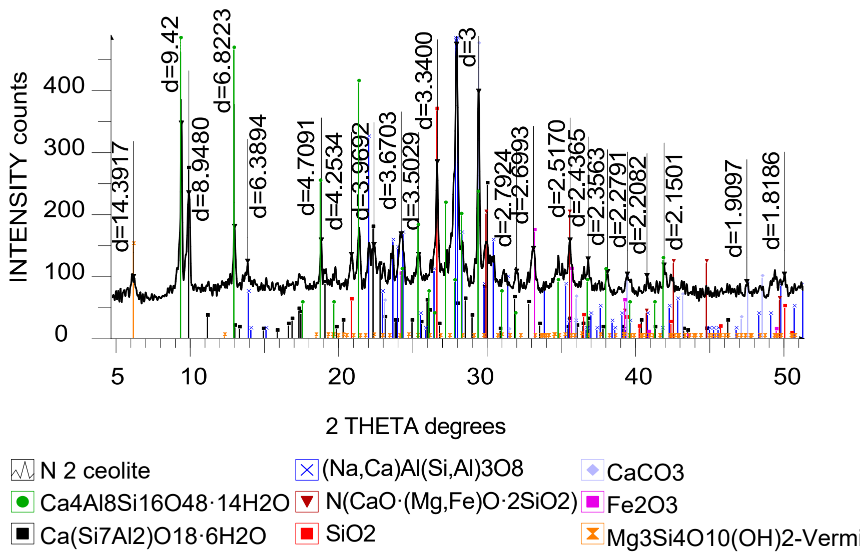

Fig. 2. X-ray of the ceolits (Maitobe field)

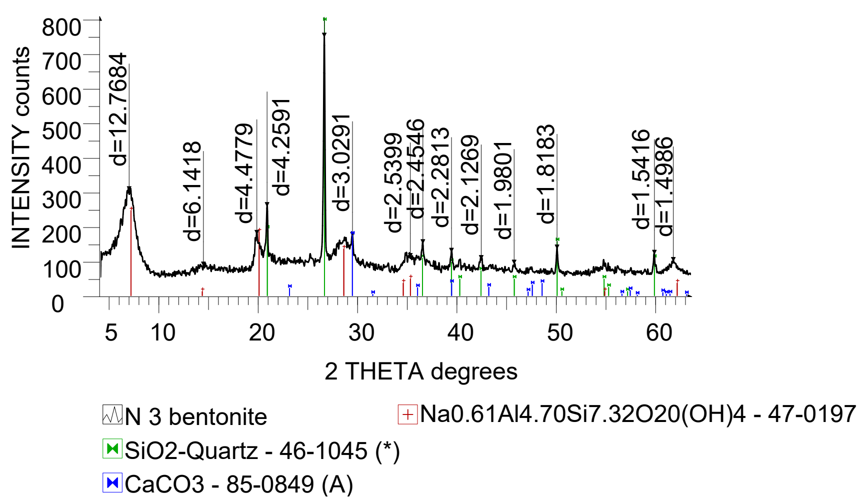

Fig. 3. Bentonite-montmorillonite sample X-ray (Middle Tentek field)

Three-layer package (2:1): two layers of silica tetrahedrons, facing their tops to each other, cover a layer of alumihydroxyl octahedres on both sides. In this connection, the connection between the packets is weak, the interpackage distance is large and it can contain ions and water molecules. Because of this, the mineral when soaking is very swollen. The presence of isomorphic substitutions, a large specific surface area (up to 600–800 m^2/g) and the ease of ion penetration into the interpackage space result in a significant cation exchange capacity (80–150 mmol equivalent/100 g).

A similar composition is found in the fourth specimen, which is the red bentonite (Mukry field) (Fig. 4). The sample contains the same Beidellite-12A – montmorillonite, as in the previous case. But the content of this smectite here is less.

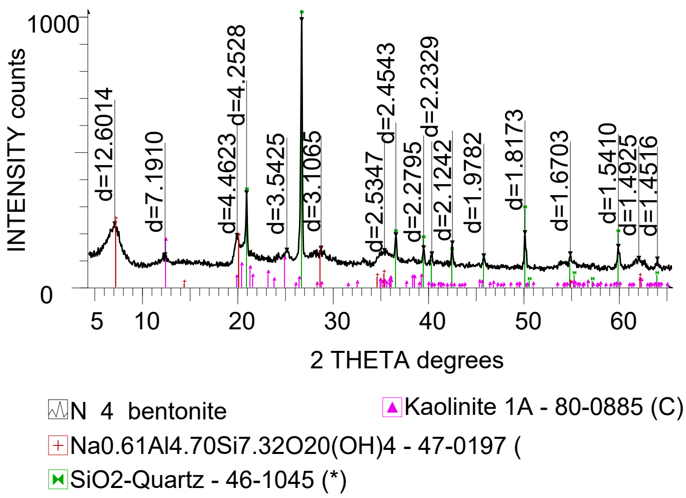

Fig. 4. Red bentonite X-ray (Mukry field)

Thus, the X-ray phase analysis gave a complete picture of the chemical composition of the materials studied. Generally speaking, the adsorption properties of these minerals are expected to be achieved due to high porosity in the case of diatomite and ceolite or the penetration of ions into the interpackage space between the bentonite layers.

5. 2. Results of the atomic-absorption study of the sorption properties of natural minerals before and after the treatment of wastewater from Pb^{+2}, Ni^{+2}, Zn^{+2} ions

Spectroscopic studies of waste water before and after treatment were carried out to study the adsorption properties of these minerals. Before studying the adsorption properties, it was necessary to analyze wastewater prior to treatment [22]. Since the wastewater under investigation is waste from the galvanic production of lead batteries, it is assumed that it contains ions of lead, zinc, nickel and other heavy metals. The main types of metal ions examined in the present paper for technical purposes are lead, zinc and nickel. Table 3 shows the content of these ions in wastewater before treatment and after treatment with limestone milk by battery plant technology.

Table 3

Results for heavy metal ions in sewage

Metal ions	Ni^{+2}, mg/dm³	Pb^{+2}, mg/dm³	Zn^{+2}, mg/dm³
Wastewater before treatment	1.801	2.465	1.347
Wastewater after treatment	0.018	0.073	0.015

As shown in Table 3, the treatment of waste water with limestone milk is quite effective. After cleaning, the content of metal ions decreases. However, according to the permissible concentration limits of pollutants in sewage, wastewater levels after limestone treatment exceed the maximum allowable concentration for these lead and nickel ions. Thus, for nickel ions the maximum permissible concentration according to this regulatory document is 0.008 mg/l, for lead ions – 0.01 mg/l, and for zinc – 0.053 mg/l.

The use of milk of lime for waste water treatment by the battery plant is based on the neutralization of acidic wastewater with alkali calcium oxide hydrate $Ca(OH)_2$. In most cases, when $Ca(OH)_2$ reacts with acids, insoluble calcium salts are formed, which, precipitating, can clog sewer networks. Therefore, after the neutralizers, sludge-fillers are provided, in which sludges are defended and the wastewater is further tempered.

At the plant, the waste water treatment is carried out in step-by-step pools, at the bottom of which the sludge is deposited. But as the data show, such cleansing is still not effective enough.

The waste water treatment was carried out as follows: samples of each adsorbent (2g) were mixed with 100 ml of wastewater taken before treatment. The resulting mixture was kept for 3 hours, with periodic mixing to improve the sorption process. After this, the filter was separated from the sediment and then diluted 100 times, depending on the contamination. Data are presented in Table 4.

The results show that the content of heavy metal ions in waste water after treatment with the adsorbents under investigation is reduced compared to waste water before treatment. Comparing adsorbents among themselves, it is possible to say that in this series bentonites manifest themselves better. Here, the content of lead, nickel and zinc ions decreases by an average of 82–85 %. If diatomite is used, the ion content of the same metals decreases by approximately 74–76 %. It's worse for zeolite. In this case, the ion concentrations detected in waste water after treatment with this adsorbent were 36 %, i. e. 64 % extraction. It should also be noted that for all adsorbents lead ions are extracted to a greater extent than other ions. This is due to the high content of this ion in the original wastewater solution.

Probably, the manifestation of higher sorption properties in bentonites is associated with their more amorphous structure, which facilitates the process of penetration of ions into the interpackage space [23].

Compared to limestone-treated waste water, the indicators shown in Table 4 for natural adsorbents were not as effective as expected.

Table 4

Co-retention of heavy metal ions in sewage by adsorption

Adsorbents/metals	C(Pb^{+2}), mg/l	C(Ni^{+2}), mg/l	C(Zn^{+2}), mg/l
Diatomite	0.614±0.098	0.448±0.071	0.335±0.053
Bentonite red	0.423±0.067	0.309±0.049	0.231±0.037
Zeolite	0.893±0.143	0.652±0.104	0.488±0.078
Bentonite montmorillonite	0.435±0.069	0.318±0.05	0.238±0.038

5. 3. Results of the kinetics of metal ion sorption by absorbent mixtures

In order to improve the quality of purification, a study of kinetics of nickel ion sorption by adsorbent mixtures was carried out. Three adsorbents were taken – diatomite, red bentonite and bentonite-montmorillonite in different ratios. The first mixture contained 30 % of diatomite and 35 % of bentonites each, and the second mixture had the same composition, but the content of diatomite was reduced to 10 % and bentonite was increased to 45 %, respectively. In addition, kinetic curves should show whether the sorption process improves over time. Fig. 5 shows the results.

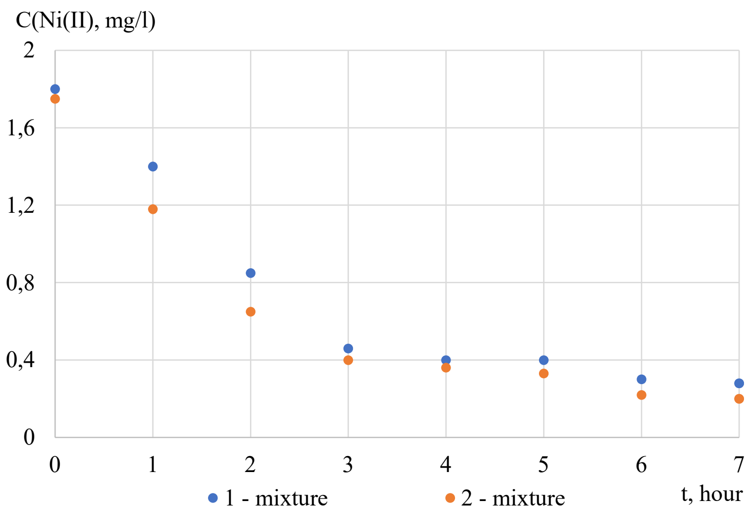

Fig. 5. Ni^{+2} ion sorption kinetics by adsorbent mixtures: 1 — mixture of composition: 30 % diatomite and 35 % red bentonite and 35 % bentonite-montmorillonite; 2 — mixture of composition: 10 % diatomite and 45 % red bentonite and 45 % bentonite-montmorillonite

The dependency of the concentration of nickel ions in the sewage after its treatment with the adsorbent mixture decreases over time to the limits that are achieved when two phases are in contact during the day. Fig. 5 shows that the adsorbent mixture with a higher bentonite content shows lower nickel ion content. Naturally, an increase in the number of bentonites, which exhibit higher sorption capacity, leads to an increased degree of nickel extraction. An intense change in the concentration of nickel ions for both mixtures is observed in the first 3 hours, then the curves go to constant values. According to the kinetic curve obtained, it can be said that practically holding the waste water with the adsorbent mixture for 3 hours is sufficient to pass the main sorption process. In principle, in 2.5–3 hours are usually physico-chemical sorption.

The next stage of the research was to test the effect of the mass of the adsorbent mixture on the efficiency of the cleaning process. For this purpose, the weight of adsorbent mixtures was increased to 4 grams. The ratio of the composition of the adsorbents remained the same. The data obtained are presented in Fig. 6, in the form of comparative charts of indicators of concentration of lead, nickel and zinc ions after treatment of waste water with individual types of adsorbents and their mixtures. As shown in Fig. 6, the lead ion content of waste water after treatment with adsorbent mixtures is reduced to 0.335 mg/l for a single mixture and to 0.268 mg/l for a two-mixture where the bentonite content is higher. These concentrations of Pb^{+2} are the lowest in the range of adsorbents used. For example, compared to the indicators for zeolite, these values are 2.5–3 times smaller. They are less than indicators for diamond almost 2 times. The adsorbent mixture is more effective in cleaning the waste water from lead ions than pure bentonites. Here, cleaning efficiency is achieved by increasing the mass of adsorbent mixtures. It would be possible to further increase the mass of adsorbents, however, an increase in the percentage weight of the absorbent material is not desirable, as this proportionally increases the weight of sludge, which is also undesirable in technological processes.

Analysis was performed with nickel ions. As shown in Fig. 6, the content of nickel ions in sewage after its treatment with adsorbent mixtures is reduced to 0.25 mg/l for a single mixture and to 0.21 mg/l for a two mixture where the bentonite content is higher. Here too, as with lead ions, the relative content of Ni^{+2} is significantly reduced compared to zeolite and diatomite.

The same pattern is observed for zinc ions (Fig. 6). Here the Zn^{+2} content in the treated waste water in the case of adsorbent mixtures is 0.25 mg/l and 0.21 mg/l. These data show that the mixtures are the best in this range of sorbents. But once again it is necessary to add that the improvement of the sorption process is due not only to the composition of adsorbents, but also to their mass.

A more clear demonstration of the effectiveness of adsorbent mixtures is Table 5, where the obtained data were used to calculate the degree of extraction of metal ions by all of the above adsorbents. The highest recovery rates are noted for lead and nickel ions when mixtures are used. The increase in the degree of extraction for the first mixture reaches 86 % and for the second mixture – 89 % for lead ions. The degree of extraction is 86 % and 88 % for nickel ions. And for zinc ions, these values reach 84 %. Thus, mixing adsorbents, increasing their mass fractions and increasing the mass of the mixture leads to a more efficient result. However, the achieved values are not sufficient for the treatment of these wastewaters, as they exceed the norms of the maximum allowable concentration.

Table 5

Degrees of extraction of metal ions by adsorbents and their mixtures

Adsorbents	Degree of extraction (Pb^{+2}), %	Degree of extraction (Ni^{+2}), %	Degree of extraction (Zn^{+2}), %
Zeolite	63.77	63.8	63.77
Diatomite	75.09	75.12	75.13
Red bentonite	82.84	82.84	82.85
Bentonite montmorillonite	82.35	82.34	82.33
1-mixture	86.41	86.12	84.11
2-mixture	89.12	88.34	84.78

Studies conducted in the work on the selection of effective natural adsorbents for the treatment of wastewater have shown that the natural materials used in the works, fields of Almaty region, have sorption capacity. The highest sorbent properties of a number of the objects studied are the bentonites, the Mukry and the Middle Tentek fields. The predominant sorption of heavy metal ions (Pb^{+2}, Ni^{+2}, Zn^{+2}) is likely to be associated with the increased ion exchange capacity of these clay minerals, due to their amorphous structure and high inflatability, which contributes to the rapid penetration of ions into the interpackage space. The lower sorption activity observed in zeolite and diatomite is probably due to the fact that the rigid frame-band structure of these minerals contains less ion-exchangeable ions.

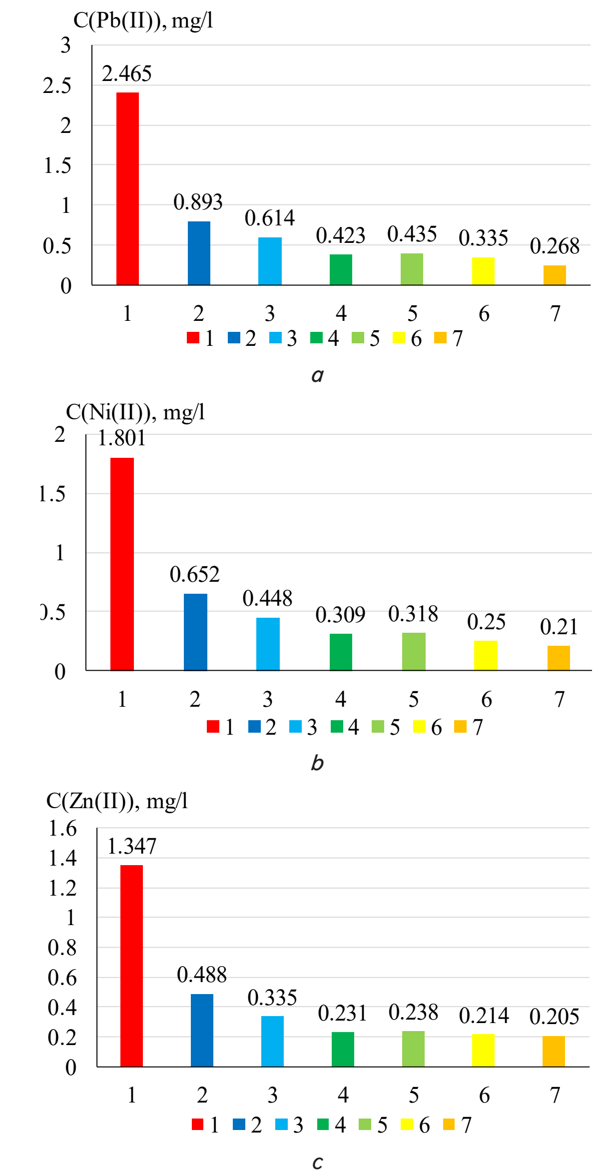

Fig. 6. Concentrations of heavy metal ions by adsorbents and mixtures: *a* – Pb(II); *b* – Ni(II); *c* – Zn(II); 1 – before cleaning, 2 – zeolite, 3 – diatomite, 4 – bentonite red, 5 – bentonite-montmorillonite, 6 – 1-mixture, 7 – 2-mixture

Studies of the kinetics of nickel ion adsorption in adsorbent mixtures showed that an increase in the bentonite mass ratio leads to an increased sorption. Significant changes in the concentration of Ni^{+2} in the test solutions occur within 3 hours, after which values decrease less sharply.

6. Discussion of the results of a study of wastewater treatment using natural sorbents

In general, the adsorption properties of these minerals are expected to be achieved by the high porosity in the case of diatomite (Fig. 1, Table 1) and zeolite (Fig. 2, Table 2) or by the penetration of ions into the underpackage space between the layers of bentonites (Fig. 3, 5).

Atomic-absorption studies carried out in the selection of effective natural adsorbents for the treatment of wastewater of the accumulator plant of "Kynar AKB", showed that the natural materials used in the work of the fields of the Almaty region have sorption capacity. Among the objects studied, the highest sorbent properties are the bentonites of the Mukra and Medium Tentec fields. The predominant sorption of heavy metal ions (Pb^{+2}, Ni^{+2}, Zn^{+2}) is likely due to the increased ionic metabolism of these clay minerals due to their amorphous structure and high swelling properties, which facilitates the rapid penetration of ions into the underpackage space (Table 4). The lower sorption activity observed in zeolite and diatomite is due to the fact that the rigid frame-zone structure of these minerals does not contain such a large amount of ions capable of ion exchange as previously shown in the work [7, 8].

A study of the kinetics of nickel ion adsorption in adsorbent mixtures showed that an increase in the mass percentage of bentonites leads to increased sorption. Significant changes in the concentration of Ni^{+2} in the test solutions occur within 3 hours, after which values decrease less sharply (Fig. 6). Increasing the weight of the adsorbent by 2 times increases the extraction of heavy metal ions from wastewater solutions to 84–89 % (Fig. 7, Table 5).

Studies have shown that natural minerals of the Almaty region have sorption properties that can be used for practical purposes, in particular for the treatment of wastewater of the accumulator plant of Kynar AKB. For practical use, holding the sewage with the adsorbent mixture for 3 hours is sufficient for the main sorption process. Increasing the weight of the adsorbent by 2 times increases the extraction of heavy metal ions from wastewater solutions. Natural adsorbents from the Almaty field can be used in acidic environment pH=1.

In the next phase of the research the authors are planning to bring the amount of sorption cleaning to the norm of maximum permissible concentration and will study the thermodynamic patterns of the sorption of ions of heavy metals.

7. Conclusions

1. X-ray phase analysis was performed to determine the chemical composition of the objects studied. A qualitative and semi-quantitative analysis of minerals was done, according to which the main component of diatomite is SiO_2, in the zeolite – Laumontite composition $Ca_4Al_8Si_{16}O_{48}{\cdot}14H_2O$ (51.3 %). The base of bentonites is bedellite-montmorillonite, which has an amorphous structure. In addition to the specified substances in the composition of these minerals there are other inclusions characteristic of mineral compounds of natural origin ($CaCO_3$, CaO, Fe_2O_3, $Mg_3Si_4O_{10}(OH)_2$).

2. Atomic-absorption spectroscopy was used to investigate the sorption of heavy metal ions (Pb^{+2}, Ni^{+2}, Zn^{+2}) by natural adsorbents. The results show that the content of heavy metal ions in waste water after treatment with the adsorbents studied decreases compared to waste water before treatment. Bentonites, Mukra and Medium Tentec have the best sorption properties. Here, the content of lead, nickel and zinc ions decreases by an average of 82–85 %. If diatomite is used, the ion content of these same metals decreases by approximately 74–76 %, and for zeolite by 64 %. The predominant sorption of heavy metal ions (Pb^{+2}, Ni^{+2}, Zn^{+2}) is likely to be associated with the increased ion exchange capacity of these clay minerals,

due to their amorphous structure and high inflatability, which contributes to the rapid penetration of ions into the interpackage space. The lower sorption activity observed in zeolite and diatomite is probably due to the fact that the rigid frame-band structure of these minerals contains less ion-exchangeable ions.

3. A study of the kinetics of nickel ion adsorption in adsorbent mixtures showed that an increase in the bentonite mass ratio leads to an increased sorption. Significant changes in the concentration of Ni^{+2} in the test solutions occur within 3 hours, after which values decrease less sharply. Increasing the weight of the adsorbent by 2 times increases the extraction of heavy metal ions from wastewater solutions. The increase in extraction rate for 1 mixture (30 % diatomite, 70 % bentonite) reaches 86 % and for 2nd mixture (10 % diatomite and 90 % bentonites) 89 % for lead ions. The extraction rate for these same mixtures is 86 % and 88 % for nickel ions, respectively. And for zinc ions, these values reach 84 %. Thus, mixing adsorbents, increasing their mass percentages and increasing the mass of the mixture leads to increased cleaning efficiency from these ions.

Conflict of interest

The authors declare that they have no conflict of interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this paper.

Financing

The study was performed without financial support.

Data availability

Data will be made available on reasonable request.

Use of artificial intelligence

The authors confirm that they did not use artificial intelligence technologies when creating the current work.

References

1. Politaeva, N., Taranovskaya, E., Mukhametova, L., Ilyashenko, S., Atamanyuk, I., Afif, R. A., Pfeifer, C. (2020). Cotton Fiber and Carbon Materials Filters for Efficient Wastewater Purification. International Journal of Technology, 11 (8), 1608. https://doi.org/10.14716/ijtech.v11i8.4538
2. Carolin, C. F., Kumar, P. S., Saravanan, A., Joshiba, G. J., Naushad, Mu. (2017). Efficient techniques for the removal of toxic heavy metals from aquatic environment: A review. Journal of Environmental Chemical Engineering, 5 (3), 2782–2799. https://doi.org/10.1016/j.jece.2017.05.029
3. Wadhawan, S., Jain, A., Nayyar, J., Mehta, S. K. (2020). Role of nanomaterials as adsorbents in heavy metal ion removal from waste water: A review. Journal of Water Process Engineering, 33, 101038. https://doi.org/10.1016/j.jwpe.2019.101038
4. Atamanova, O. V., Tichomirova, E. I., Politayeva, N. A., Podolsky, A. L., Istrashkina, M. V. (2019). Innovative technologies for industrial wastewater treatment. IOP Conference Series: Earth and Environmental Science, 288 (1), 012001. https://doi.org/10.1088/1755-1315/288/1/012001
5. Kuznetsova, E., Akulova, A., Motovilov, A. (2016). Problems and solutions for processing and disposal of sewage galvanic production. Eurasian Union of Scientists, 3 (24), 109–112.
6. Atamanova, O., Tikhomirova, E., Koshelev, A., Istrashkina, M., Politayeva, N., Podolsky, A. (2019). Wastewater treatment of industrial enterprises via adsorption method. IOP Conference Series: Earth and Environmental Science, 337 (1), 012010. https://doi.org/10.1088/1755-1315/337/1/012010
7. Boriskov, D., Efremova, S., Komarova, N., Tikhomirova, E., Bodrov, A. (2021). Applicability of the modified diatomite for treatment of wastewater containing heavy metals. E3S Web of Conferences, 247, 01052. https://doi.org/10.1051/e3sconf/202124701052
8. Obuzdina, M., Rush, E. (2019). New sorption materials based on modification of natural zeolites in metal wastewater treatment processes. E3S Web of Conferences, 140, 08001. https://doi.org/10.1051/e3sconf/201914008001
9. Veprikova, E. V., Tereshchenkoa, E. A., Chesnokova, N. V., Shchipkova, M. L., Kuznetsova, B. N. (2010). Features of water purification from petroleum products using petroleum sorbents, filter materials and active carbons. Filtering Materials and Active Coals Journal of Siberian Federal University, 3 (3), 285–304.
10. Feofanov, Yu. A., Mishukov, B. G., Podporin, A. V., Feofanov, M. Yu. (2017). Evaluation of the effectiveness of the use of various sorption materials for cleaning of oil-containing water. Water Magazine, 5 (117).
11. Petukhova, Yu. N., Ilyina, S. I., Fursenko, A. V., Nosyrev, M. A. (2019). Ochistka stochnyh vod ot ionov tyazhelyh metallov s pomoshch'yu sorbentov. EurasianUnionScientists, 6 (64). https://doi.org/10.31618/esu.2413-9335.2019.6.64.254
12. Kurilina, T. A., Andreeva, S. A., Kurilin, S. S. (2016). Sorption of heavy metal ions from aqueous solutions with a modified sorbent. Eurasian Union of Scientists, 1 (22), 26–29.
13. Surkova, T., Abdikerim, B., Berkinbayeva, A., Azlan, M. N., Baltabekova, Zh. A. (2022). Obtaining modified sorbents based on natural raw materials of Kazakhstan and research of their properties. Kompleksnoe Ispol'zovanie Mineral'nogo

Syr'â/Complex Use of Mineral Resources/Mineraldik Shikisattardy Keshendi Paidalanu, 322 (3), 23–32. https://doi.org/10.31643/2022/6445.25

14. Dehmani, Y., Ba Mohammed, B., Oukhrib, R., Dehbi, A., Lamhasni, T., Brahmi, Y. et al. (2024). Adsorption of various inorganic and organic pollutants by natural and synthetic zeolites: A critical review. Arabian Journal of Chemistry, 17 (1), 105474. https://doi.org/10.1016/j.arabjc.2023.105474
15. Mudaber, S Batur, J. (2023). Differences in Heavy Metals Adsorption on Natural, Modified, and Synthetic Zeolites-A Review. Journal of the Turkish Chemical Society Section A: Chemistry, 10 (3), 847–860. https://doi.org/10.18596/jotcsa.1263041
16. Bikulova, V. Zh., Latypova, F. M., Mukhametdinova, L. Kh. (2013). Adsorption treatment of industrial wastewater from zinc ions. Technologies of Industrial and Domestic Water Treatment, 3, 37–39.
17. Gholikandi, G. B., Baneshi, M. M., Dehghanifard, E., Salehi, S., Yari, A. R. (2010). Natural zeolites application as sustainable adsorbent for heavy metals removal from drinking water. Iranian J. of Toxicology, 3 (3), 302–310. Available at: http://ijt.arakmu.ac.ir/article-1-53-en.html
18. Ju, O., Ibe, E. (2014). Adsorption studies of heavy metals by low-cost adsorbents. J. Appl. Sci. Environ. Manage, 18 (3), 443–448. Available at: http://www.bioline.org.br/pdf?ja14060
19. Surchi, K. M. S. (2011). Agricultural Wastes as Low Cost Adsorbents for Pb Removal: Kinetics, Equilibrium and Thermodynamics. International Journal of Chemistry, 3 (3). https://doi.org/10.5539/ijc.v3n3p103
20. Khadhraoui, M., Watanabe, T., Kuroda, M. (2002). The effect of the physical structure of a porous Ca-based sorbent on its phosphorus removal capacity. Water Research, 36 (15), 3711–3718. https://doi.org/10.1016/s0043-1354(02)00096-9
21. Khraisheh, M. A. M., Al-Ghouti, M. A., Allen, S. J., Ahmad, M. N. M. (2004). The Effect of pH, Temperature, and Molecular Size on the Removal of Dyes from Textile Effluent Using Manganese Oxides-Modified Diatomite. Water Environment Research, 76 (7), 2655–2663. https://doi.org/10.1002/j.1554-7531.2004.tb00227.x
22. Zhao, G. (2011). Sorption of Heavy Metal Ions from Aqueous Solutions: A Review. The Open Colloid Science Journal, 4 (1), 19–31. https://doi.org/10.2174/1876530001104010019
23. Bokiev, B., Khujaev, P., Sharipov, Sh., Murodov, P. (2018). Sorption method for purification of industrial wastewater waters. Bulletin of Science and Practice, 4 (7), 203–209.