

New magnetic clays MnFe₂O₄/Shymkent for removal of heavy metals from wastewater

Zhaina Baimuratova^{1,*}, Sayat Ermekov², Adriano Silva³, Hélder Gomes³, and Marzhan Kalmakhanova¹

¹M. Kh. Dulaty Taraz Regional University, Taraz, Kazakhstan

²M. Auezov South Kazakhstan University, Shymkent, Kazakhstan

³Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Bragança, Portugal

Abstract. This paper reports the development of a new method. Production of modified clay with magnetic properties based on natural clay from the Shymkent deposit (MnFe₂O₄/Shymkent nanocomposite), determination of its chemical composition and structure, as well as the study of basic physicochemical properties. The resulting magnetic nanocomposite was then used as an adsorbent to remove nickel (II) ions from wastewater. The prepared magnetic nano composite was then used as adsorbent to remove Ni (II) ions from wastewater, and the optimal conditions for determining thermodynamic and kinetic parameters were evaluated. It was determined that the natural clay from the Shymkent deposit is a promising material for the modification of the materials. The advantage of such magnetic adsorbents in comparison with the natural materials used as adsorbents is their higher adsorption capacity and the ability to control them using a magnetic field. To characterize the modified adsorbents, various assays were used, such as EMP and XRD analysis. The textural properties of the materials were determined by analyzing N₂ adsorption-desorption isotherms at 77 K. It is shown that almost all textural and adsorption characteristics of MnFe₂O₄/Shymkent have significantly improved as a result of the modification made. It was concluded that the MnFe₂O₄/Shymkent adsorbent obtained in the work can be used for effective wastewater treatment to remove nickel ions.

1 Introduction

Kazakhstan's waterways are alarmed at their "polluted" fate. Ecologists from the Ministry of Environmental Protection (MEP) noted in the latest edition of the ministry's newsletter: Out of 69 rivers in Kazakhstan, only 9 are considered clean. The other 60 are contaminated. About 80 water bodies in Kazakhstan are polluted to varying degrees by various chemicals and substances. The rapid development of the economy and industry leaves deep scars on the pristine "face" of the blue lakes and rapid rivers of Kazakhstan. Discharges of various wastes into water bodies occur at the same rate, and sewage flows into lakes and rivers in multiple streams [1].

* Corresponding author: jaina.baimuratova@mail.ru

The amount of water pollution is constantly increasing. The self-purifying ability of water is sometimes insufficient to cope with the growing amount of waste. Under the influence of currents, pollution spreads very quickly, adversely affecting areas rich in fauna and flora, causing serious damage to marine ecosystems and the economy as a whole. Water pollution and purification is one of the most pressing problems for many countries in the world, especially for Kazakhstan. Water consumption increases every year, and fresh water supplies on the planet are limited. [2].

The removal of various toxins from water and wastewater has received much attention from scientists and the world in recent years. Paint manufacturing, battery manufacturing, printing industry, mining, metallurgical engineering, electroplating, pigments, PVC stabilizers, nuclear power, electrical equipment manufacturing, semiconductor, cosmetics and other industries that produce various types of pollutants in wastewater [3,4].

Heavy metals pose a serious environmental problem due to their toxicity and abundance. It is known that the presence of heavy metals in the aquatic environment causes a number of health problems for humans and animals [5]. Heavy metals are an important group of inorganic pollutants and contaminate much of the world through soil, fertilizers, pesticides, household waste, and residues from mining and metallurgical industries [6]. Many heavy metals are known to be carcinogenic and can pose a serious threat to living humans due to their non-destructive, stable and accumulative nature [7-9].

Various remediation technologies used to remove heavy metals include chemical precipitation, ion exchange, chemical oxidation, reduction, reverse osmosis, ultrafiltration, electrodialysis and adsorption. Of these methods, adsorption is the most effective since other methods have inherent limitations such as large amounts of sediment formation, low efficiency, sensitive operating conditions and expensive disposal, and the associated high costs are a limiting factor in their commercialization.

In recent years, adsorption has become a promising solution for removing heavy metal ions as the simplest, most economical and environmentally friendly method. Adsorption is the most common method at present due to the design flexibility, simplicity of equipment manufacturing, installation and operation, allowing high-quality and reversible wastewater treatment, as well as the lower associated costs. In addition, the adsorbent can be regenerated [10].

To contribute to the improvement of wastewater adsorption solutions, there is an urgent need to study cheaper, natural, environmentally friendly and effective adsorbing materials. The use of local natural clays as adsorbents was considered earlier in other works for wastewater treatment and removal of heavy metals [11].

Natural clay minerals (NCMs) have attracted a lot of attention due to their special properties and their use in a wide range of industrial and environmental applications. The economic benefits are obvious because NCMs is widely available and inexpensive compared to other raw materials. For these reasons, research at the NCMs is actively conducted by many scientists from many countries, and the future of clay science seems interesting and promising.

The chemical and physical properties of specific substances depend on their composition and structure. [12].

Clays has exchangeable cations and anions on its surface, and for this reason, scientific attention worldwide has focused on the use of natural or modified clay materials as adsorbents for water purification [13]. Most clay minerals have a negative charge and are very effective and widely used for adsorption of metal cations from solution, due to their high cation exchange capability, high surface area and volume of pores. The adsorption of heavy metals by clay minerals comprises a number of complex adsorption mechanisms, such as direct binding of metal cations to the surface of clay minerals, surface complexation and ion exchange, among others [14].

The development of methods to obtain nanoscale particles make it possible to produce new materials based on them, with the necessary properties for use in various industries. Nanoscale adsorbents also include magnetite (Fe_3O_4) nanoparticles, dispersion and high specific surface areas, that allow to consider these materials as incomparable adsorbents. The structure and movement of magnetite nanoparticles can be regulated by an external magnetic field. For this reason, their scope of application is very extensive. An effective method of obtaining magnetic adsorbents is the introduction of magnetite into the clay structure. The convenience of using clay minerals as frameworks is justified by their porosity and interplane structure, which allows them to immobilize or even synthesize magnetite particles. The magnetic composition of clays retains its lyophilicity, unlike individual magnetites, and this determines the stability of their suspensions. It has been reported that heavy metal ions with a positive charge are well adsorbed in clay minerals with a negative charge. As the adsorption surface shifts to a negative value, the adsorption capacity increases. Adsorption of heavy metals in clay-magnetite composites consists of two main interactions: the mechanism of ion exchange by SiOH -groups and the formation of chelate complexes with surface hydroxyl groups of the mineral [15].

In many studies, a pretreatment is required to increase the adsorption capacity of clays and, therefore, modification is performed to increase metal adsorption [16]. This pretreatment increases the surface area, pore volume and the number of acidic functionalities present on the surface. Due to such processing or modification, clay minerals become hydrophobic, organophilic, enhancing the adsorption of small nonionic organic compounds [17]. Thus, the use of clay and its materials would solve the problem of recycling, as well as provide access to less expensive material for wastewater treatment.

The purpose of this work is to study natural clay minerals, as well as to obtain magnetic composites ($\text{MnFe}_2\text{O}_4/\text{clay}$) using as precursors natural clays of the Shymkent deposit, Kazakhstan. The adsorbent materials are then used for the removal of Ni(II) from wastewater. Also, the effect of the clay adsorbent dose, pH, initial concentration of metal ions and contact time was investigated.

2 Experimental

2.1. Materials and synthesis of magnetic materials

Natural clay minerals of the Shymkent deposit were considered in the study.

The following reagents were used to modify the clay: sodium hydroxide (NaOH , purity ≥ 0.97), iron(III) sulfate nonahydrate ($\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$, purity ≥ 0.98), manganese chloride tetrahydrate ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, purity ≥ 0.99), Nickel sulfate heptahydrate ($\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, purity ≥ 0.99). A model solution (50 mg/L) containing Ni(II) ions was prepared by dissolving a certain amount of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ in distilled water.

For the synthesis of the modified clay, An aqueous solution containing manganese (II) and iron (III) in a molar ratio of 1:2 was prepared. Then 5 g of prepared clay was added to the solution and mixed to obtain Fe^{+3} and Mn^{+2} ions located on the surface layers of clay. Then a sodium hydroxide solution (5 mol/L) was added to bring the pH to 10, and the resulting solution was stirred at 25 °C for 30 minutes using a magnetic stirrer. After that, the resulting suspension was heated to 95-100 °C. After cooling for 2 hours, the prepared magnetic mixture was washed again with warm water at a temperature of 50 °C. Then the resulting material was separated from the water and could be dried in the oven at a temperature of 105 °C for 2 hours until completely dehydrated. The resulting mixture was added at a temperature of 400 °C to the muffle furnace for 3 hours to give the material new properties. When heated to a high temperature, volatile impurities are removed from the

material, and their oxidation and destruction completely hydrate the material in preparation for use as an absorbent.

2.2 Characterization

To characterize the adsorbent materials, various analyzes were carried out, and the composition of natural materials and modified clay was determined by EMP. X-ray diffraction analysis was carried out on a DRON-3 automatic detector equipped with a CuK α radiation and a β filter. Special conditions of the diffraction method: U=35 kV; i = 20 mA; shooting θ -2 θ ; Find 2 degrees per minute.

The properties of the products were determined by analyzing the N₂ adsorption-desorption isotherm at 77 K, obtained on a Quanta Chrome NOVATOUCH XL4 adsorption analyzer using the same method [18]. Briefly, the material was annealed at 120°C for 16 hours and then the specific area was determined using the beta method and the Langmuir method (SBET, SLangmuir). The total pore volume (V total) was determined at $p/p^\circ = 0.98$. All calculations using these methods were carried out using Touch WinTM software v1.21.

Thermogravimetric was carried out at the MOM derivatograph - Budapest (Hungary). The method is used to record changes in the thermochemical and physical parameters of a substance caused by heating. The thermochemical state of the sample is described by the following curves: T (temperature), DTA (differential thermoanalytical), TG (thermogravimetric) and DTG (differential thermogravimetric), the curve of the second derivative of the TG function.

Adsorption was carried out for 8 hours, samples were taken at intervals of 15, 30, 60, 120, 240, 360 and 480 minutes. Ni(II) concentration was determined using AES. All measurements were performed using an Agilent 4200 MP-AES equipped with an Agilent 4107 nitrogen generator. The sample injection system consisted of a two-pass cyclone nebulizer, Neb nebulizer, Solvaflex pump tube (orange/green), and one nebulizer. To install the injection test burner. A multi-element calibration standard containing Ni(II) at a concentration of 50 mg/L was used. Standards were prepared from a mixture of 5% HNO₃/0.2% HF (v/v) (made in the USA).

3 Results and discussion

3.1. X-RAY diffractometric analysis

The X-ray diffractograms of natural clay Shymkent deposit and modified clay is shown in figures 1 and 2. X-ray phase analysis is carried out on a semi-quantitative basis by diffraction of powder samples on the same installation using X-ray diffraction methods. The synthesis is perfect. The size of the crystalline phase was calculated. Diffraction patterns were determined using data from the ICDD: Powder Diffraction Database PDF2 file (Powder Diffraction File) and diffraction patterns of non-contaminant metals. Potential impurities, clear identification due to low concentration and presence of only 1-2 diffraction reflections, lack of chemical data, poor structure or crystallization are listed in Tables 1 and 2.

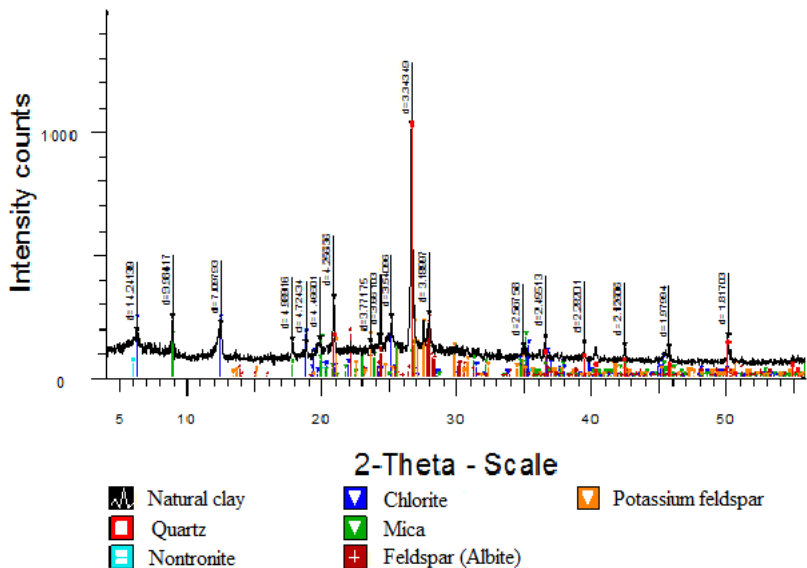


Fig. 1. Diffraction pattern of natural clay of the Shymkent deposit.

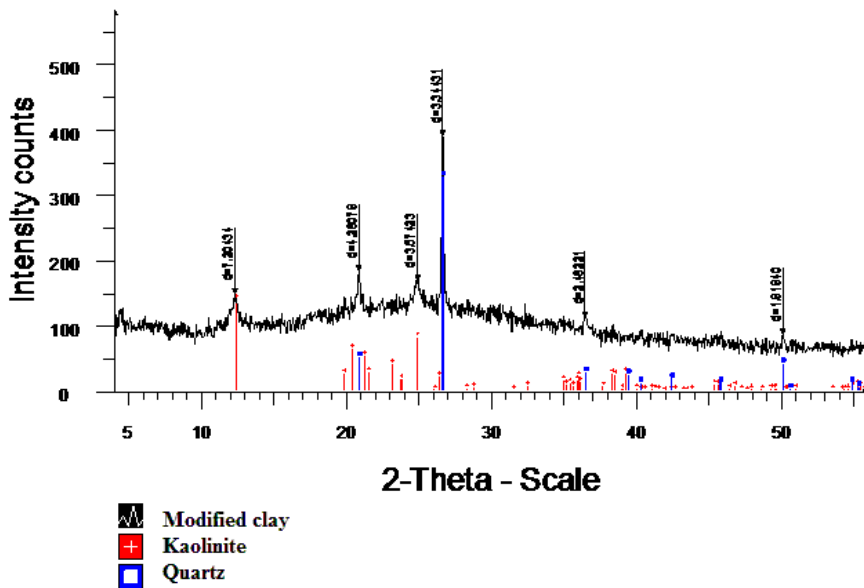


Fig. 2. Diffractogram of modified clay MnFe₂O₄/ Shymkent.

Table 1. Results of semi-quantitative X-ray phase analysis of natural clays of the Shymkent deposit.

Mineral	Formula	Concentration, %
quartz	SiO ₂	42.0
nontronite	(Fe,Al)Si ₂ O ₅ (OH)·H ₂ O	29.2
chlorite	(Mg,Fe) ₅ Al(Si ₃ Al)O ₁₀ (OH) ₈	9.8
mica	KAl ₂ (AlSi ₃ O ₁₀)(OH) ₂	7.1
albite (Feldspar)	Na(AlSi ₃ O ₈)	6.7
Potassium Feldspar	KAlSi ₃ O ₈	5.2

Table 2. Results of semi-quantitative X-ray phase analysis of the modified clay MnFe₂O₄/Shymkent.

Mineral	Formula	Concentration, %
quartz	SiO ₂	32.7
kaolinite	Al ₂ (Si ₂ O ₅)(OH) ₄	67.3

3.2. Elemental Composition

The results of the composition of natural soil elements and amendments were obtained by EMP analysis (Fig. 3). Table 3 shows the content of elements in natural and modified clay. As already noted, Shymkent is rich in iron (6.23%), silicon (28.66%) and aluminum (9.83%), which corresponds to the phase identified in the clay sample (Table 1). In the clay modified with MnFe₂O₄, the Fe content increased compared to natural clay, which indicates the exchange and fixation of the metal intercalated in the interlayer space. In the MnFe₂O₄/Shymkent 15.04% of Fe and 10.83% Mn is observed.

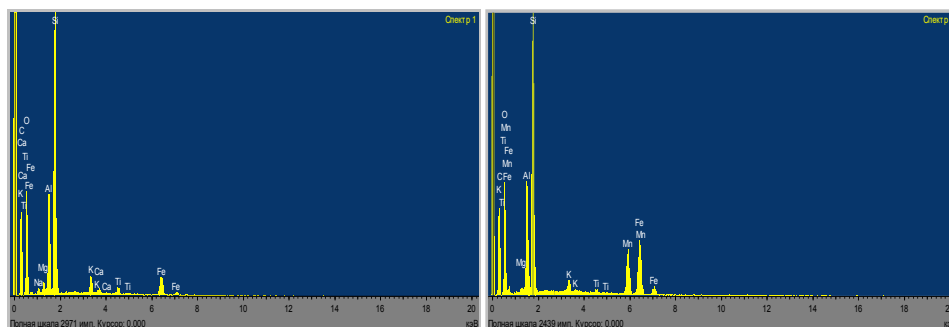


Fig. 3. Elemental composition and microstructure of a sample of a) natural clay of the Shymkent deposit and b) MnFe₂O₄/Shymkent.

Table 3. Elemental composition of the natural and modified clays.

Clay	Element weight (%)									
	O	Na	Mg	Al	Si	K	Ca	Ti	Mn	Fe
Shymkent	49.28	0.87	1.19	9.83	28.66	2.16	0.52	1.27	-	6.23
MnFe ₂ O ₄ /Shymkent	36.19	-	0.56	9.80	25.71	1.40	-	0.47	10.83	15.04

3.3. N₂ Adsorption desorption isotherms at 77 K

The composition of the material was determined based on the analysis of N₂ adsorption-desorption isotherms at 77 K, presented in Figure 4. The composition of the material is summarized in Table 4.

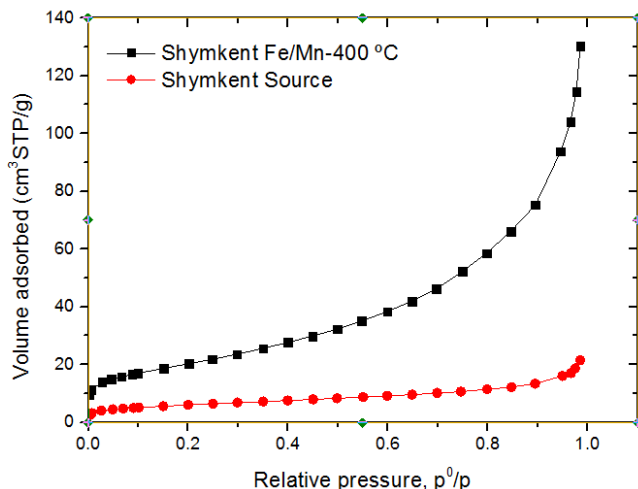


Fig. 4. N₂ adsorption isotherms at 77K of the natural clay and modified clay of the Shymkent deposit.

Table 4. Textural properties of materials.

Sample	S _{BET} (m ² g ⁻¹)	S _{Langmuir} (m ² g ⁻¹)	V _{Total} (cm ³ g ⁻¹)
"MnFe ₂ O ₄ /Shymkent, 400 °C	74	81	1.77
Shymkent Source	21	25	0.029

3.4. Thermal analysis (DTA and TGA)

The results of the thermal analysis (DTA and TGA) of the natural clay of the Shymkent deposit are shown in Fig. 5 and in Tables 5 and 6.

The analysis were carried out in air environment at temperatures from 20 to 1000°C. The fire heating mode is linear (dT/dt = 10°C/min), for clarity, the reference substance is Al₂O₃. Example of a 200 mg firing position with a sensitivity of 100 mg The analysis was carried out within the following limits of the device’s measurement system: DTA = 250 μV, DTG = 500 μV, TG = 500 μV, T = 500 μV

The sample and the reference substance for analysis were placed in ceramic crucibles.

As a result of dynamic heating of these samples, the curves DTA, DTG and TG noted manifestations caused by the occurrence of various types of reactions in the system. Among them are processes connected with the release H₂O and hydroxyls into the atmosphere during the decomposition of clay minerals.

The natural clay from the Shymkent deposit, when heated in a dynamic mode, left pronounced manifestations on the thermal curves connected with decomposition reactions of a group of minerals that make up the desired sample. As a result of the decomposition of thermally active inclusions of the tested natural formation, endothermic peaks formed on the DTA curve at 115 and 445 °C due to the thermal destruction of hydromica, montmorillonite and kaolinite, Table 6. As a result of the decomposition of these clay minerals, the mass loss phases Δm₁, Δm₂ and Δm₃ remained on the thermogravimetric TG curve, and three weak depressions formed on the DTG line, two of which (at 80 and 440°C) correspond in intensity to the peaks of the DTA curve.

The reaction occurring within the rangof 20-200°C is caused by dehydration of montmorillonite and hydromica. Moreover, two-thirds of the mass of lost water in this temperature range comes from montmorillonite and one-third from the hydrate difference of

mica. The next stage of dehydration of these minerals is fixed within 200-350°C, where hydroxyl water leaves the system in the amount of $\Delta m_2 = 0.625\%$ of the initial weight of the sample. Here, the fraction of the ejected montmorillonite OH is 0.4% of the mass of the sample, and the fraction of the ejected hydromica OH accounts for 0.225%.

Thus, according to the established weight losses caused by the removal of the molecular form of water and hydroxyl from the system, as well as taking into account the stoichiometric formulas of these minerals, the content of montmorillonite and of hydromicas in the sample corresponds to 10% and 7.7%, respectively (Tables 5 and 6).

Thermal destruction of kaolinite, in contrast to these clay minerals, proceeds in one stage, when hydroxyls, as an element of the structure of this mineral, break their bonds and go beyond the influence of the forces of the crystal lattice. The dynamics of the destruction of the structure corresponds to the rate of exit of OH-groups from it. The temperature range (345-600°C) in which the dehydroxylation of the mineral is carried out, and the programmable rate of temperature rise (10 °C/min) in the charge under study are the temperature-chronological conditions of the decay period of the tested kaolinite. According to the results of dehydration of the specified object, and its stoichiometric data, the amount of kaolinite in the sample is 10%. Chlorite, in thermal terms, is a poorly informative mineral. In multi component clay formations, this representative of layered silicates is often found. As a result, the weight loss ($\Delta m_3 = 0.5\%$) noted in the range of 600-1000°C, where dissociation of chlorite usually occurs, should be attributed to the dehydration of this mineral. Due to its low content in the sample, the endothermic effect on the DTA curve is hidden by the background of high-temperature thermal interference accompanying the processes of structural transformations of the object under study. Thus, using the value of Δm_3 and the stoichiometric formula of chlorite, , an amount of 4.2% was obtained.

Along with the minerals of layered silicates, the presence of silica (a group of thermally inactive minerals), quartz, was found in the sample. This mineral undergoes a reversible polymorphic transformation when heated in the 500°C region. In the vicinity of this temperature, quartz gives a very weak endothermic effect of the transition of its structure from the α -state to the β -modification. As a rule, the endothermic effect is below the level of thermal noise and interference from neighboring thermally active inclusions – in this case, the endothermic peak (on the DTA curve) of the destruction of kaolinite completely overlaps the temperature zone of the thermal manifestation of quartz.

In this regard, it is not possible to simultaneously trace the presence of the quartz and kaolinite effect. A weak quartz effect could be detected during secondary heating of the sample, i.e. during calcination of the firing product of the initial clay, when the kaolinite decay reaction has already been abolished. Thus, a very weak effect of the supposed quartz was detected. According to the intensity of the established peak of the polymorphic transformation of SiO₂ and the residual principle, it was determined that the quartz content in the sample, with an accuracy of $\pm 10\%$, is $\sim 40\%$. Other components of the sample include thermally inert substances that do not manifest their presence during firing. Their number is calculated according to the residual principle. It corresponds to $\sim 28\%$. These include free oxides (mainly silicon dioxide) and minerals, in the structures of which there are no thermally active components.

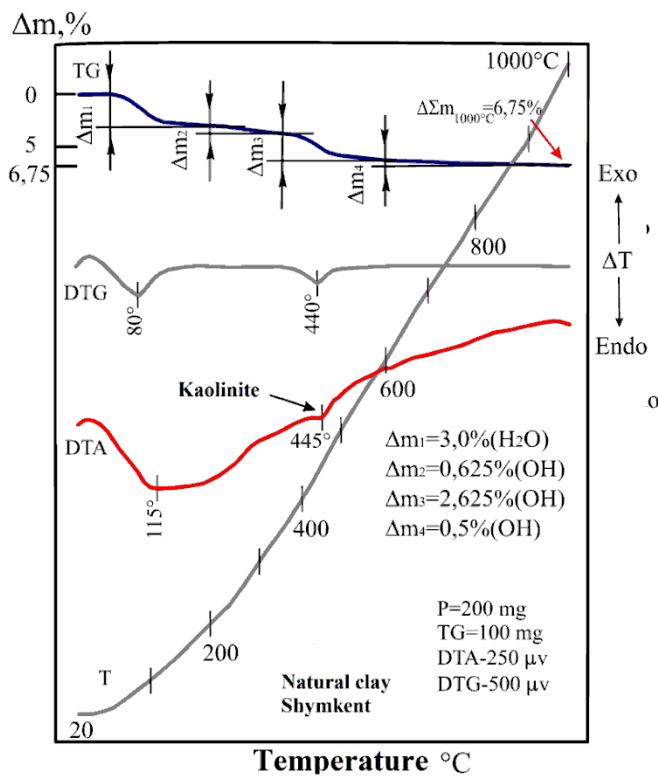


Fig. 5. Derivatogram of the natural clay from the deposits of Shymkent.

Table 5. Thermogravimetric readings of the natural clay from the deposits of Shymkent in the range of 20-1000 °C

Weight reduction sequence	Amount of weight loss, in %	Volatile constituents of the heated sample	Thermal range of the decomposition stage, °C
Δm_1	3,0	H ₂ O	20-200
Δm_2	0,625	OH	200-350
Δm_3	2,625	OH	350-600
Δm_4	0,5	OH	600-1000
$\Sigma \Delta m_{1000^\circ C}$	6,75	H ₂ O, OH	20-1000

Table 6. Mineral and material composition of a sample of natural clay Shymkent, in % according to thermal analysis.

Mineral and materia lcomposition	%
Quartz	~40
Montmorillonite	10
Kaolinite	10
Hydromica	7.7
Chlorite	4.2
Thermally inert substances	~28

The results of the thermal analysis (DTA and TGA) of the modified clay are shown in Figure 6 and in Tables 7 and 8. It is observed that MnFe₂O₄/Shymkent, when heated, registers on its curves all the same manifestations that were observed during the firing of the original natural clay. A significant difference in the development of these reactions in the

upgraded clay is the increased intensity of their course, Figure 6. So, on the DTA and DTG curves of MnFe₂O₄/Shymkent, the peak amplitudes associated with the dehydration of montmorillonite, hydromica and kaolinite, noticeably exceed the corresponding amplitudes noted on the curves of the natural clay from the Shymkent deposit. Similar changes in favor of increasing all stages of weight loss are demonstrated by the thermogravimetric (TG) curve of the test sample, as shown in Table 7. It can be seen that in each temperature range, in which the dehydration reactions of the upgraded clay occur, more water is released into the atmosphere than was traced during the firing of the original natural clay.

Since the content of clay minerals in the sample was controlled by the amount of H₂O and OH released into the atmosphere, the calculated amount of montmorillonite, hydromica, kaolinite and chlorite in the modified MnFe₂O₄/Shymkent samples was higher than the original natural composition. the clay in the sample is given in Table8.

An increase in the amount of finely dispersed clay minerals in the sample leads to a corresponding decrease in the content of coarse fractions in the sample, which include quartz and thermally inert formations. The quartz content was determined by the same method as in the case of the natural clay from the Shymkent deposit. The amount of it in the upgraded clay ranges from ~ 25%. The content of thermally inert inclusions in the composition of the studied sample corresponds to <15%, as given in Table 8.

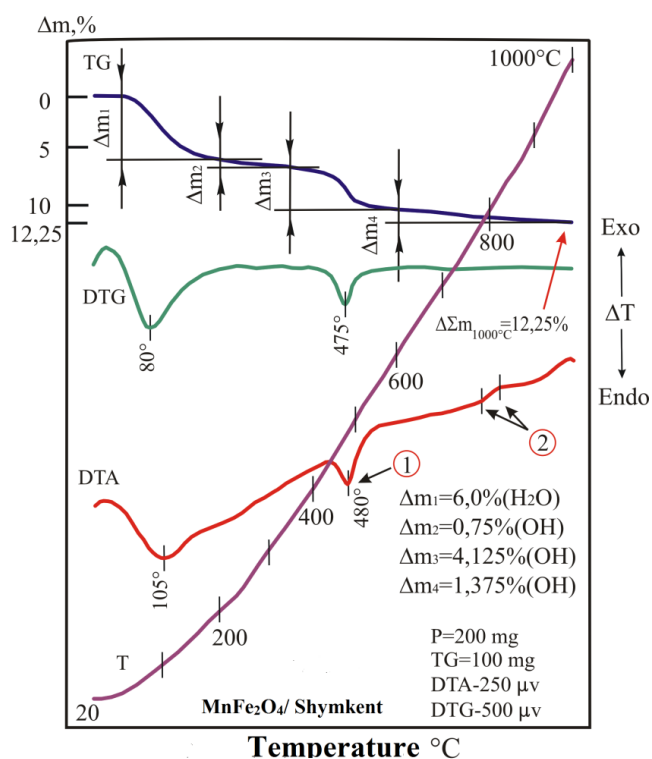


Fig. 6. Derivatogram of the modified clay MnFe₂O₄/ Shymkent. 1- endothermic peak of kaolinite; 2 - decomposition of chlorite

Table 7. Thermogravimetric readings of the modified clay MnFe₂O₄/Shymkent, in the range f 20-1000 °C.

Weight reduction sequence	Amount of weight loss, in %	Volatile constituents of the heated sample	Thermal range of the decomposition stage, °C
Δm ₁	6,0	H ₂ O	20-200
Δm ₂	0,75	OH	200-345
Δm ₃	4,125	OH	345-600
Δm ₄	1,375	OH	600-1000
ΣΔm _{1000°C}	12,25	H ₂ O, OH	20-1000

Table 8. Mineral and material composition of MnFe₂O₄/ Shymkent sample, in % according to thermal analysis.

Mineral and material composition	%
Quartz	~25
Montmorillonite	19.6
Kaolinite	15.7
Hydromica	16.9
Chlorite	5.8
Thermally inert substances	~17

3.5. Adsorption runs

The adsorption efficiency when using the same adsorbent depends on the initial concentration of pollutant in the solution, temperature, pH of the solution, residence time, dose of adsorbent and dimensional parameters of the adsorbent.

When wastewater is purified from heavy metals by adsorption, the pH value of the solution significantly affects the degree of purification. In this work, the dependence of the adsorption capacity of Ni(II) ions with an increase in the pH of the solution over the adsorption time was considered. The results obtained are shown in Figure 7 and summarized in Table 9.

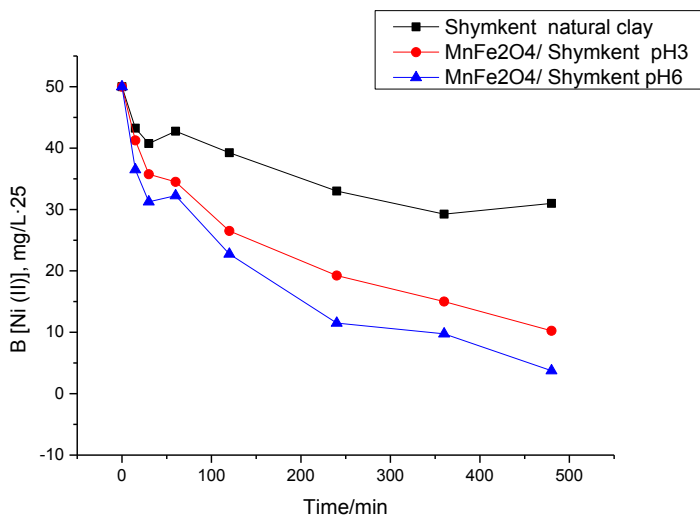


Fig. 7. The effect of contact time and pH on the removal of Ni (II) by adsorption of the natural clay from the Shymkent deposit and the modified MnFe₂O₄/Shymkent.

Conditions: Ni(II) concentration = 50 mg/L, 2.5 g/L adsorbent, pH 3.0 and pH 6.0

Table 9. Results of analysis of the effect of adsorption time and pH on the adsorption process.

Adsorbent	Time of adsorption, min	pH	[Ni (II)]mg/L
Shymkent natural clay	0	3	50
	15		43.25
	30		40.75
	60		42.75
	120		39.25
	240		33
	360		29.25
	480		31
MnFe ₂ O ₄ / Shymkent	0	3	50
	15		41.25
	30		35.75
	60		34.5
	120		26.5
	240		19.25
	360		15
	480		10.25
MnFe ₂ O ₄ / Shymkent	0	6	50
	15		36.5
	30		31.25
	60		32.25
	120		22.75
	240		11.5
	360		9.75
	480		3.75

Based on the results obtained, adsorption with the natural clay is passive compared to that observed with the modified MnFe₂O₄/Shymkentclay. The results of nickel adsorption using natural clay showed that after 8 hours, the percentage of adsorbed heavy metal was only 35.4%, while with the modified clay, at pH3 showed 78.5% of adsorbed nickel in 8 hours. The best result was shown by MnFe₂O₄/Shymkentat pH 6, the percentage of adsorbed nickel for 8 hours being 92.1%. Analysis of the results obtained clearly emphasizes that modified clays have much higher adsorption capacity than natural clays with respect to nickel removal. The natural clay has shown good potential for removing nickel from the model solution, without any modifications, however, their removal ability has been improved by modification. Such processing methods as chemical, physical (thermal), mechanochemistry and combined impregnation have been successfully used to modify the natural clay of the Shymkent deposit in order to improve its ability to absorb heavy metals. The interaction of time, as well as modified clay and MnFe₂O₄/Shymkent during the removal of Ni(II), PH

removal is influenced by the efficiency of pH6, and the efficiency of pH3 is less than significantly higher than it has been proven.

4 Conclusion

Clay minerals can effectively adsorb pollutants from water effluents due to their good adsorption capacity and high cation exchange capacity. However, naturally occurring clay materials with hydrophilic properties are not particularly effective for removing heavy metals. Therefore, in this paper, the issue of hydrophilicity is solved by modifying clays to obtain and increase their adsorption capacity with respect to heavy metal cations.

Modified MnFe₂O₄/Shymkent clays were tested for their ability as adsorbents. MnFe₂O₄/Shymkent showed high adsorption characteristics for the removal of the heavy metal Ni(II) from model waters. Time-dependent adsorption experiments showed that the rate of Ni(II) adsorption on modified clay was high, the maximum amounts of Ni(II) being adsorbed in the range from 15 minutes to 8 hours of contact time. Thus, clays modified by magnetic particles are an excellent choice as economical and effective adsorbents for water purification from heavy metals.

This research is funded by the Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan (Grant No. AP13067715) and by Base Funding of CIMO (UIDB/00690/2020) through FEDER under Program PT2020.

References

1. "Oko" Newspaper, <https://online.zakon.kz>
2. A. S. Balykbaeva, "Report "Pollution of water resources of Kazakhstan and methods of water purification", in Republican pedagogical journal "OQU-ZAMAN" (2017)
3. I. Ali, V. K. Gupta, *Nat. Protoc.* **1**, 2661–2667 (2007)
4. V. K. Gupta, P. J. M. Carrott, M. M. L. Ribeiro Carrott, *Crit. Rev. Environ.Sci. Technol.* **39**, 783–842 (2009)
5. M. Alkan, M. Dogan, *J. Colloid InterfaceSci.* **243**, 280–291 (2001)
6. M. Halim, P. Conte, A. Piccolo, *Chemosphere* **52**, 26–75 (2002)
7. R. Balasubramanian, S. V. Perumal, K. Vijayaraghavan, *Ind. Eng. Chem. Res.* **48**, 2093–2099 (2009)
8. V. K. Gupta, I. Ali, *J. Colloid Interface Sci.* **271**, 321–328 (2004)
9. R. A. K. Rao, M. Kashifuddin, *Appl. Water Sci.* **4**, 371–383 (2014)
10. Fenglian Fu, Qi Wang, *Journal of Environmental Management* **92(3)**, 407–418 (2011)
11. M. I. Khan, M. K. Almesfer, M. Danish, I. H. Ali, H. Shoukry, R. Patel, J. Gardy, A. S. Nizami, M. Rehan, *Desalination and Water Treatment* **158**, 140-151 (2019)
12. Aref Alshameri, Xinghu Wei, Hailong Wang, Yang Fuguo, Xin Chen, Hongping He, Chunjie Yan, Feng Xu, A Review of the Role of Natural Clay Minerals as Effective Adsorbents and an Alternative Source of Minerals [http](http://www.sciencedirect.com/science/article/pii/S2214717019300011) (2019)
13. R. Srinivasan, *Adv. Mater. Sci. Eng.* **2011**, 1–17 (2011)
14. G. Churchman, W. Gates, B. Theng, G. Yuan, *Handbook of Clay Science: Developments in Clay Science* **1(11.1)**, 625-675 (2006)
15. G. Kurmangazy, Sorption properties of magnetic clays: prepared dissertation for the degree of Doctor of Philosophy (PhD) (2020)

16. D. W. O’Connell, C. Birkinshaw, T. F. O’Dwyer, *Bioresour. Technol.* **99**, 6709–6724 (2008)
17. S. Ismadji, F. E. Soetaredjo, A. Ayucitra, Clay Materials for Environmental Remediation, in *Springer Briefs in Green Chemistry for Sustainability*
18. Zh. A. Baimuratova, M. S. Kalmakhanova, Sh. S. Shynazbekova, N. S. Kybyraeva, J. L. Diaz de Tuesta, H. T. Gomes, *News of the national academy of sciences of the Republic of Kazakhstan series of Geology and Technical Sciences* **2(452)**, 58-72 (2022)