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Satbayev University

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$MnFe_2O_4$/ZHETISAY COMPOSITE AS A NOVEL MAGNETIC MATERIAL FOR ADSORPTION OF Ni(II)

Abstract. This paper deals with the preparation of magnetic adsorbents from natural clays for the adsorption of Ni(II) from aqueous matrices. The phase composition and structure parameters of natural clays and their modified forms, as well as their application as adsorbing agents for the purification of drinking water and their sources were studied. In the study, natural clays from the Zhetisay deposit of Kazakhstan were used to obtain magnetic composites by chemical co-precipitation and applied as effective adsorbents to remove Ni(II) from water. The formation of sorbents by magnetic nanoparticles is an urgent task of our time. This is due to the needs of various branches of science and technology in magnetically controlled sorbents. The advantage of such sorbents in comparison with natural sorbents is the ability to control them using a magnetic field. Sorbents with magnetic properties are used for contact cleaning of substances, which greatly simplifies the sorption process and the completeness of the sorbent processing. The use of such materials makes it possible to replace the mechanical separation stage, which is one of the labor-intensive stages of this process.

Magnetic pillared clays were obtained by intercalation of iron and manganese cations in the region between the clay silicate layers, upon hydrolysis of a solution of $Fe_2(SO_4)_3 \cdot 9H_2O$ and $MnCl_2 \cdot 4H_2O$ with NaOH. The intercalated clay is then dried and calcined at 400°C for 3 h.

The basic physical and chemical properties were stu died by XRD, elemental analysis, FTIR and atomic emission spectral analysis (AES). The obtained magnetic pillared clays ($MnFe_2O_4$/Zhetisay) showed better characteristics than natural clays. The results of adsorption revealed that the optimal adsorption conditions were observed at pH 6.

Key words: heavy metal,magnetic pillared clays, adsorption,modification, intercalation, water treatment.

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MNFE2O4/ZHETISAY КОМПОЗИТІ NI(II) АДСОРБЦИЯСЫ ҮШІН ЖАҢА МАГНИТТІК МАТЕРИАЛ РЕТІНДЕ

Аннотация. Бұл мақалада табиғи саздардан магниттік композиттерді синтездеудің жаңа әдісінің дамуы сипатталған. Табиғи саздардың фазалық құрамы мен құрылымының параметрлері және олардың модификацияланған формалары, сондай-ақ ауыз су мен олардың көздерін тазарту үшін адсорбциялық агент ретінде қолдану зерттелді. Зерттеуде Қазақстандағы Жетісай кен орнынан табиғи саздар химиялық бірлесіп тұнбаға түсіру жолымен магниттік композиттер алу үшін пайдаланылды және Ni(II) судан жою үшін тиімді адсорбенттер ретінде пайдаланылды. Магнитті нанобөлшектердің көмегімен сорбенттерді әзірлеу біздің заманымыздың өзекті мәселесі болып табылады. Бұл магнитпен басқарылатын сорбенттегі ғылым мен техниканың әртүрлі салаларының қажеттіліктеріне байланысты. Мұндай сорбенттердің табиғи сорбенттермен салыстырғанда артықшылығы – оларды магнит өрісінің көмегімен басқару мүмкіндігі. Магниттік қасиеттері бар сорбенттер жанаспалы тазалау үшін пайдаланылады, бұл сорбция процесін және сорбентті өңдеудің толықтығын айтарлықтай жеңілдетеді. Мұндай материалдарды пайдалану механикалық бөлу сатысын алмастыруға мүмкіндік береді, бұл осы процестің ауыр кезеңдерінің бірі. Магнитті бағаналы саздар $Fe_2(SO_4)_3 \cdot 9H_2O$ және $MnCl_2 \cdot 4H_2O$ ерітінділердің NaOH-мен гидролизі кезінде сазды силикат қабаттары арасындағы

аймақтағы темір катиондарын интеркаляциясы арқылы алынды. Содан кейін интеркалирленген саз кептіріліп, 3 сағат ішінде 400°C температурада қыздырылды.

Ауыз суды тазарту кезінде химиялық құрамы мен құрылымы, сондай-ақ табиғи және модификацияланған саздардың адсорбциясының тиімділігі қолданыстағы технологиялармен, материалдармен және әдістермен салыстырғанда едәуір жоғары екендігі анықталды. Негізгі физикалық және химиялық қасиеттері XRD, элементтік талдау, FTIR және атомдық эмиссиялық спектрлік талдау (АЭС) арқылы зерттелді. Алынған магниттік бағаналы саздар ($MnFe_2O_4$/Жетісай) табиғи саздарға қарағанда жақсы сипаттамаларды көрсетті. Адсорбция нәтижелері pH6 кезінде оңтайлы адсорбция жағдайлары сақталғанын көрсетті. Ni(II) адсорбциясының оңтайлы тиімділігі 5 мг/л концентрациясында болды.

Түйін сөздер: ауыр металл, магниттік бағаналы саз, адсорбция, модификация, интеркаляция, суды тазарту.

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КОМПОЗИТ MnFe2O4/ZHETISAY В КАЧЕСТВЕ НОВОГО МАГНИТНОГО МАТЕРИАЛА ДЛЯ АДСОРБЦИИ Ni(II)

Аннотация. В данной статье описывается разработка нового метода синтеза магнитных композитов из природных глин. Были изучены параметры фазового состава и структуры природных глин и их модифицированных форм, а также их применение в качестве адсорбирующих агентов для очистки питьевой воды и их источников. В исследовании природные глины с месторождения Жетисай в Казахстане использовались для получения магнитных композитов путем химического совместного осаждения и применялись в качестве эффективных адсорбентов для удаления Ni(II) из воды. Формирование сорбентов с помощью магнитных наночастиц является актуальной задачей нашего времени. Это связано с потребностями различных отраслей науки и техники в магнитоуправляемых сорбентах. Преимуществом таких сорбентов по сравнению с природными сорбентами является возможность управлять ими с помощью магнитного поля. Сорбенты с магнитными свойствами используются для контактной очистки веществ, что значительно упрощает процесс сорбции и полноту обработки сорбента. Использование таких материалов позволяет заменить стадию механического разделения, которая является одной из трудоемких стадий этого процесса.

Магнитные столбчатые глины были получены путем интеркалирования катионов железа в области между слоями глинистого силиката при гидролизе раствора $Fe_2(SO_4)_3$•$9H_2O$ и $MnCl_2$•$4H_2O$ с NaOH. Затем интеркалированную глину сушат и прокаливают при 400°C в течение 3 часов.Установлено, что химический состав и структура, а также эффективность адсорбции природных и модифицированных глин при очистке питьевой воды по сравнению с существующими технологиями, материалами и методами значительно выше. Основные физические и химические свойства были изучены с помощью XRD, элементного анализа, FTIR и атомно-эмиссионного спектрального анализа (АЭС). Полученные магнитные столбчатые глины с ($MnFe_2O_4$/Жетисай) показали лучшие характеристики, чем природные глины. Результаты адсорбции показали, что оптимальные условия адсорбции соблюдались при pH 6. Оптимальная эффективность адсорбции Ni(II) была при концентрации 5 мг/л.

Ключевые слова: тяжелый металл, магнитные столбчатые глины, адсорбция, модификация, интеркаляция, очистка воды.

Introduction. Most heavy metal ions enter the environment by anthropogenic means, mainly from the emissions of mining and processing enterprises, as well as from thermal power plants. The most voluminous source of pollution is wastewater, which is drained into surface reservoirs with an insufficient level of purification. The second sourceof heavy metals introduction in nature is through flue gases, which are deposited on the earth surface and washed away into water sources. Another source, perhaps the most serious type of pollution, is originated in the water that is formed when mine workings are flooded. In this case, even underground water is polluted (Kuzminchuk Anna, 2019).

The maximum risk of poisoning with heavy metal ions occurs when using water from surface reservoirs and wells without subsequent treatment. In cases where underground water is contaminated, it is also not recommended to consume water from wells. This applies to the industrial regions of Southern Kazakhstan. Water treatment has been a required technology in many industries, because water contamination and pollution have become major environmental problems worldwide. This has created a great demand for an effective water treatment technology, and adsorption is the most popular technique due to their easy handling. Adsorption is also more economical than other techniques. Magnetic materials, especially iron-based particles, have been known to have characteristic properties for specified applications, including for water treatment (Anderson N.J., 1982)

Natural clays are inexpensive and readily available materials that function as excellent cation exchangers. The adsorption capacity of clays is due to the relatively high surface area and net negative charge in their structure, which attracts and holds cations such as heavy metals (Khenifi A., 2007), (Wu R. 2005). The application of magnetic particle technology to solve environmental problems is also considered. Magnetic particles can be used to adsorb pollutants from water or gaseous effluents and, after adsorption, the adsorbent can be separated from the medium by a simple magnetic process. Therefore, there is a growing interest in low-cost materials with a high surface area, especially metal oxides, due to their unique applications, including adsorption and chemical catalysis (Oliveira L.C. 2003).

The city of Zhetisay in the Turkestan region is rich in mineral resources, which largely ensure the socio-economic development of the region. The main mineral wealth are non-metallic minerals (chalk, clay, sand, apatite). Clays are products of rock erosion found widely distributed in nature. Their chemical and textural composition varies from one place to another, depending on their geological origin and the presence of organic and inorganic impurities (Rouquerol J. 2014). Natural clays are abundantly available low-cost natural resources, and nontoxic to ecosystem. Over the recent years, there has been research on the modification of clays to increase their adsorbent capacity to remove contaminants from drinking water (Reimbaeva, 2020).

To produce magnetic nanoparticles in aqueous clay mineral dispersions, the co-precipitation method can be used, based on the chemical reaction to promote the in situ nucleation and growth of nanoparticles in the aqueous dispersion of clay minerals, as described in Figure 1. The synthesis of nanocomposites by co-precipitation involves mixing the clay mineral with magnetic nanoparticle (MNP) precursors under alkaline condition to form a sol–gel system. NaOH is commonly used to create the alkaline condition, which directly produces the precipitate of the composite (Orolínová, 2009), (Tokarčíková, 2017), (Zong, 2013). The interaction between MNP produced from clay minerals in a sol–gel system can be intensified using several methods, such as heating in a reflux system or microwave-irradiation. As the precipitate is created, drying or calcination can be conducted, influencing the iron oxide phase and magnetization properties through various processes.

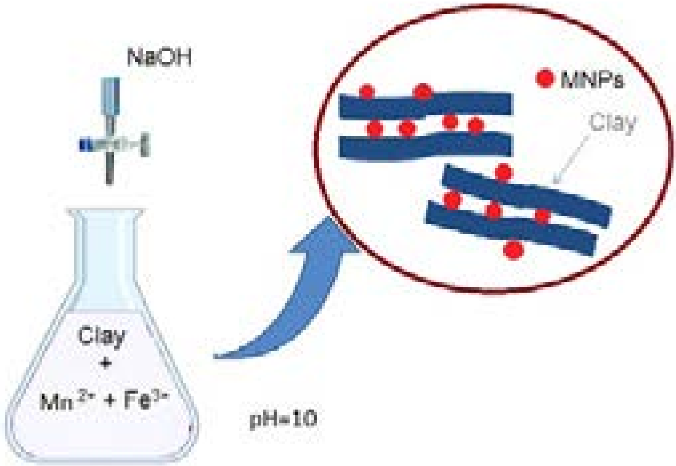


Figure 1. Schematic representation of the co-precipitation method.

Pillarization is another method of nanocomposite formation (Figure 2). In pillarization, MNPs are formed by intercalation of oxides or precursors of iron and manganese into the interlayer structure of smectite clay, followed by a calcination step (400°C).

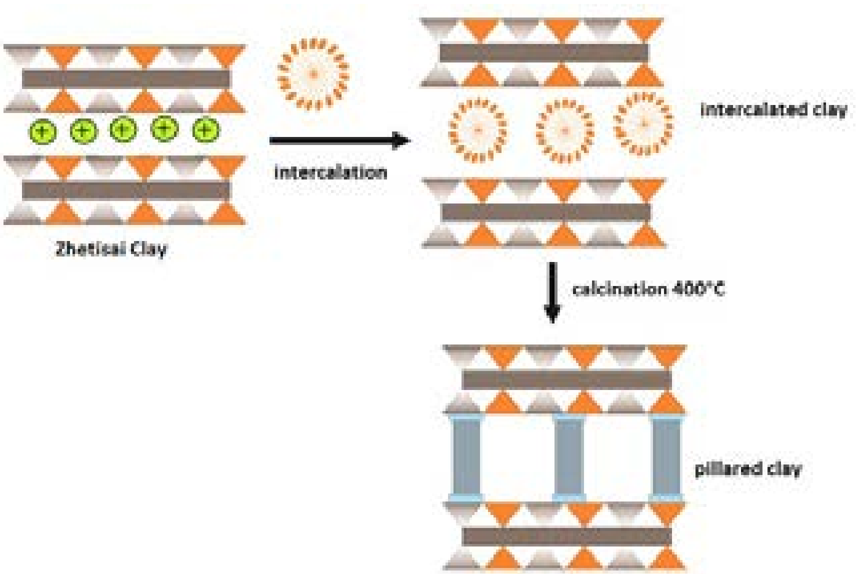


Figure 2. Schematic representation of clay pillarization.

Adsorption from aqueous solutions of electrolytes occurs, as a rule, in such a way that mainly ions of the same type are adsorbed on the solid adsorbent from the solution. The predominant adsorption from a solution of either anion or cation is determined by the nature of the adsorbent and of the ions (Prokhina, 2013), (Shapovalov, 2010).

Combining the adsorption properties of clay minerals with the magnetic properties of MNPs to produce new $MnFe_2O_4$/Zhetisay clay adsorbents is a promising method for the removal of pollutants from water.

In practice, several factors influence intensive adsorption, such as pH, adsorbent dosage, time of treatment, among others.

The aim of this work is to synthesize and study the peformance of natural clays and a magnetic pillared clay ($MnFe_2O_4$/Zhetisay) as adsorbents for the removal of Ni(II)from water.

Materials and methods. The clays studied in this work were obtained from the Zhetisay deposit in Kazakhstan. Sodium hydroxide (NaOH, purity ≥ 0.97), iron(III) sulfate nonahydrate ($Fe_2(SO_4)_3 \cdot 9H_2O$, purity ≥ 0.98), manganese chloride tetrahydrate ($MnCl_2 \cdot 4H_2O$, purity ≥ 0.99), nickel sulfate heptahydrate ($NiSO_4 \cdot 7H_2O$, purity ≥ 0.99). It is worth noting that all chemicals were used in this study without further purification.

Synthesis of magnetic materials. Due to the suitable clay mineral adsorption properties, the increase of adsorption capacity can be improved by enhancement of clay material porosity after chemical and physical treatments. Inorganic acid activation, bases, salts, thermal treatment, pillaring by different polyhydroxy cations, polymer-modified clays and surfactants have been used for the modification of clay minerals. For the preparation of the magnetic pillared clay $MnFe_2O_4$/Zhetisay, the zhetisay natural clay was previously grinded into powder in a mill and sorted through a sieve size of 0,063 mm. To prepare the magnetic composite $MnFe_2O_4$/Zhetisay, an aqueous solution containing manganese(II) and iron(III) in a molar ratio of 1:2 was prepared. Then 5g of the prepared clays were added to the solution, followed by mixing to obtain Fe^{3+} and Mn^{2+} ions located on the surface layers of the clay.

A solution of sodium hydroxide (5 mol/L) was further added to bring the pH value to 10. The resulting solution was then stirred for 30 minutes on a magnetic stirrer at room temperature. Next, the suspension was heated to 95-100°C and the prepared magnetic composite was washed with distilled water at 50°C for 2 h. Using a simple magnetic procedure, the obtained materials were separated from water and dried in oven at a temperature of 105°C for 2 h. The resulting composite was further calcined at 400°C for 3 hin a muffle furnace to give the substance new properties. By heating to high temperatures, volatile impurities are removed from the materials and its oxidation and brittleness leads to completely dehydrated materials, becoming ready for use as an adsorbent.

Characterization. To characterize the adsorbents various analyses were performed. X-ray diffractometric (XRD) analysis were carried out on an automated DRON – 3 diffractometer with Cu_K-radiation and a β-filter. Conditions for shooting diffractograms were U=35 kV; I=20 mA; shooting θ-2θ; detector 2 deg/min.Fourier Transform Infrared Spectroscopy (FT-IR) was performed on a spectrometer INFRASPEC FSM2202. The IR spectra of all compounds were recorded in solid form in KBr tablets. The results on elemental composition of the natural clays were obtained by EMP analysis. The iron content in the samples was determined by atomic absorption using the AAS-3 spectrophotometer. The apparent volume of the sediment was measured in 25 mL measuring tubes with a division of 0.1 mL.

The concentration of Ni(II) was determined by AES. All measurements were carried out using the Agilent 4200 MP-AES fitted with the Agilent 4107 Nitrogen Generator. The sample introduction system consisted of a double pass cyclonic spray chamber, one Neb nebulizer, Solvaflex pump tube (orange/green) and an Easy-fit torch to introduce the sample. Multi-element calibration standards containing Ni(II) with a concentration of 50 mg/L were used. The standards were prepared in a 5% HNO_3/0.2% HF (v/v) medium (Made in USA).

The textural properties of the materials were determined from N_2 adsorption–desorption isotherms at 77 K, obtained in a Quantachrome NOVATOUCH XL[4] adsorption analyser, following the same procedure as reported Briefly, the degasification of the samples was conducted at 120ºC during 16 h and then BET and Langmuir specific surface area (S_{BET}, $S_{Langmuir}$) were determined using BET and Langmuir methods, respectively. The total pore volume (V_{Total}) was determined at p/p^0 = 0.98. Calculations of those methods were done by using TouchWin™ software v1.21.

Results and discussion. X-ray phase analysis on a semi-quantitative basis was performed using diffractograms of powder samples using the method of equal attachments and artificial mixtures. The results obtained are shown in Figure 3. The quantitative ratios of the crystal phases were determined. The interpretation of the diffractograms was carried out using data from the ICDD card file: the PDF2 Powder diffraction data base (Powder Diffraction File) and diffractograms of minerals free of impurities. Shooting conditions were DRON diffractometer-3.0, accelerating voltage-35 kV and anode current = 20mA.

The result of the analysis established that the sample of the studied Zhetisay clay belongs to the group of layered silicates-kaolinite $Al_2(Si_2O_5)(OH)_4$ and mixed-layer clay minerals (MCM) K-Na-Al-Si-O-(OH) (Table 1).

Table 1. Results of semi-quantitative x-ray phase analysis of Zhetisay natural clay

Mineral	Formula	Concentration(%)
Quartz	SiO_2	52.9

Kaolinite	$Al_2(Si_2O_5)(OH)_4$	22.1
MCM	K-Na-Al-Si-O-(OH)	19.7
Mica	$KAl_2(AlSi_3O_{10})(OH)_2$	5.3

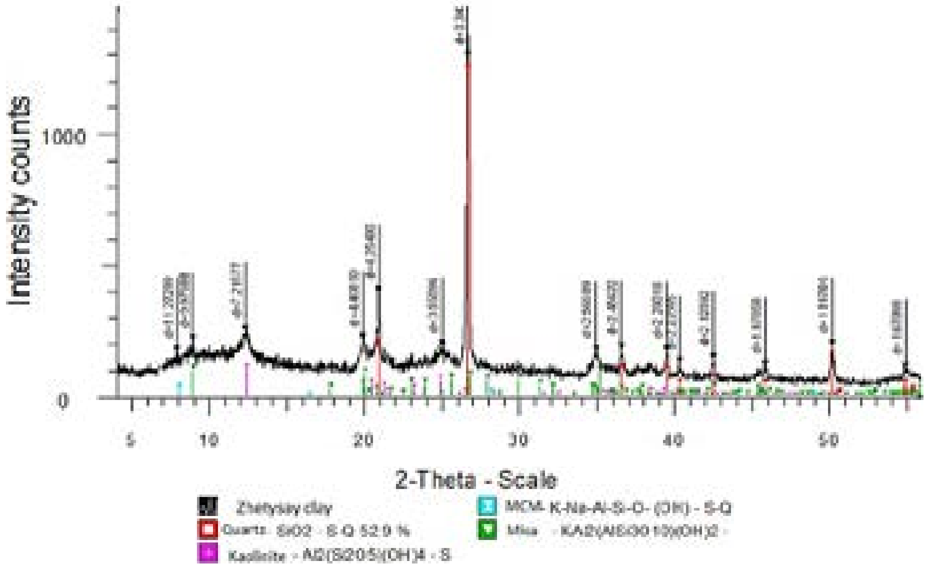
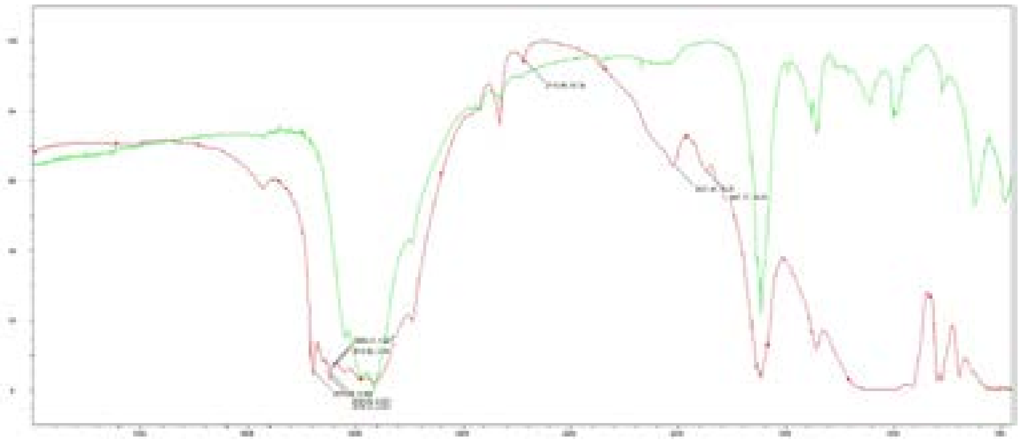


Figure 3. Diffractogram of the Zhetisay natural clay.

The analysis of the IR spectra of the Zhetisay clay is shown in Figure 4a, revealing that the main bands in the natural clay are related to the valence bonds of silicon with oxygen and hydrogen with oxygen. The spectra of the Zhetisay clay is quite complex, the intensity and position of the IR absorption bands depend on the conditions of the formation of the mineral and on the presence of various ions-impurity elements (Mg, Ca, Fe) in the crystal lattice of the mineral. With an increase in the ionic radius of the cation in the mineral, the peaks shift to a longer wavelength region. By comparison of the infrared spectra of various modifications of clay minerals it is possible to identify and evaluate the influence of the structure of minerals on the pattern of these spectra. The most diagnostic bands of the Zhetisay clay studied in our work are those appearing at 3701 cm^{-1}, 3616 cm^{-1} and 3605 $cm^{-1}$for kaolinite ($Al_2(Si_2O_5)(OH)_4$), and the absorption bands at 2713$cm^{-1}$and 2021cm^{-1} that allow identifying mica in the clay ($Kal_2(AlSi_3O_{10})(OH)_2$), which is also confirmed by X-ray phase analysis. In the clay samples, absorption bands of 457 cm^{-1}, 794cm^{-1}, 1035cm^{-1} and 3695cm^{-1} are observed, which, according to the database, corresponds to MCM (K-Na-Al-Si-O- (OH)) and quartz SiO_2.

a)



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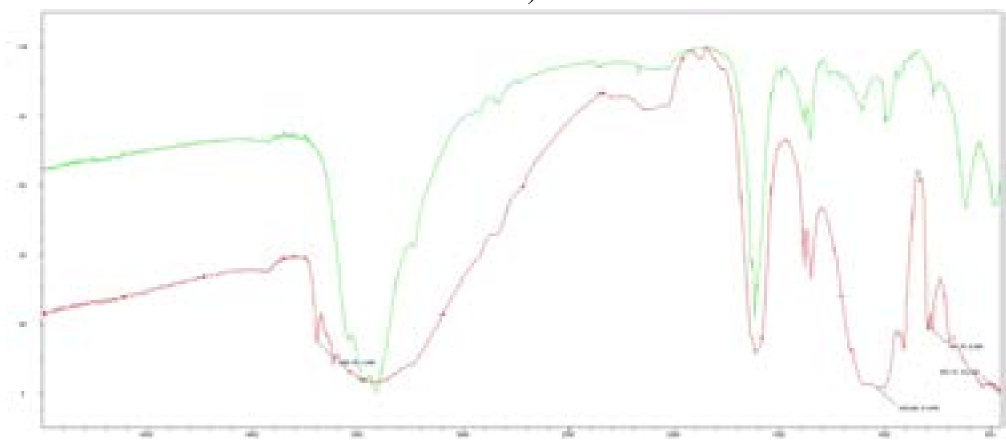


Figure 4. FTIR spectrum of a) Zhetisay natural clay, b) $MnFe_2O_4$/Zhetisay.

Table 2 shows the content of elements in the natural clay, obtained by elemental analysis. As noted, in the clay sample, Zhetisay is rich in aluminum (11.5%) and silicium (28.9%).

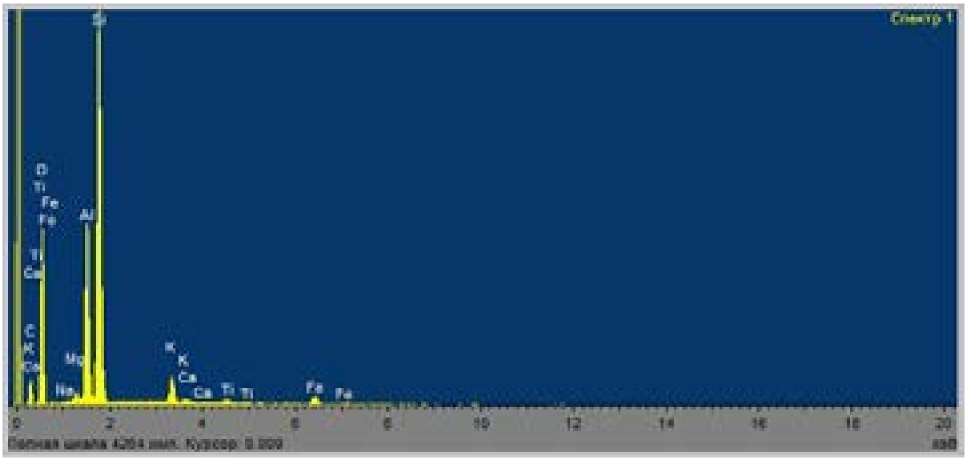
Table 2. Elemental composition of the Zhetisay natural clay and of $MnFe_2O_4$/Zhetisay.

Clay	Weight of the element (%)									
	O	Na	Mg	Al	Si	K	Ca	Ti	Mn	Fe
Zhetisay natural clay	53.7	0.1	0.8	11.5	28.9	2.5	0.1	0.5	0.0	1.9
$MnFe_2O_4$/ Zhetisay	44.2	0.2	0.5	6.8	18.7	1.5	0.2	0.3	8.0	19.6

The results show that in the modified $MnFe_2O_4$/Zhetisay, the Fe content increases in comparison with the natural clay, which indicates the exchange and fixation of intercalating metals in the interlayer space, with corresponding reduction of Al and Si contents. In the $MnFe_2O_4$/Zhetisay, Fe amounts to 19,6% and the Mn content also reached 8.0% (Table 2).

The results of elemental composition of the natural and modified clays were obtained using EMP analysis (Figure 5).

a)



b)

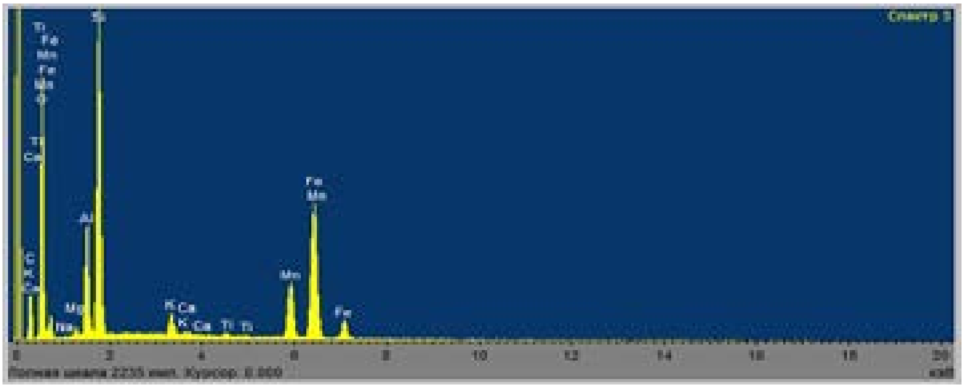


Figure 5. Elemental analysis of a) Zhetisay natural clay, b) $MnFe_2O_4$/Zhetisay.

Textural properties of the clays. Figure 6 shows theN_2 adsorption isotherms at 77 K of the prepared materials. As observed, the modified $MnFe_2O_4$/Zhetisay has a higher N_2 adsorption than the Zhetisay source precursor used. Comparison of the adsorption behavior of both materials becomes more understandable from the calculated textural properties (Jose, 2018), (Jose et al. 2021) given in Table 3. As can be seen, $MnFe_2O_4$/Zhetisay shows the highest specific surface area (S_{BET}= 89m^2/g, $S_{Langmuir}$= 95 m^2/g, S_{ext} = 89 m^2/g) and total pore volume showed a value of 1.59 cm^3/g.Thus, Zhetisay natural clay is promising for the production of porous materials.

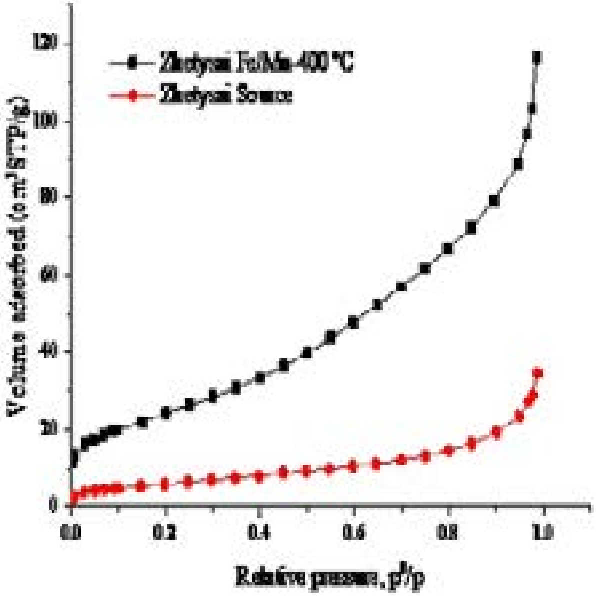


Figure 6. N_2 adsorption isotherms at 77 K of the materials.

Table 3.

Textural properties of the materials.

Clay	S_{BET} (m^2/g)	$S_{Langmuir}$ (m^2/g)	S_{ext} (m^2/g)	V_{mic} (cm^3/g)	V_{total} (cm^3/g)
Zhetisay natural clay	89	95	89	0	1.59
$MnFe_2O_4$/Zhetisay	22	24	22	0	4.46

Ni(II) adsorption performance. The efficiency of adsorption when using the same adsorbent depends on the initial concentration of the solution, temperature, pH of the solution, residence time, dose of adsorbent and dimensional parameters of the adsorbent.

When water sourcesare treated from heavy metals by adsorption, the pH value of thesolution significantly affects the degree of purification. In this work, the dependence of the degree of adsorption of Ni(II) ions with an increase in the pH of the solution along adsorption time was considered. The results obtained are gathered in Table 4. The adsorption was carried out for 8 h, samples for analysis were taken at intervals of 15-30 minutes and 1-2 hours. The results are also shown in Fig. 7.

At pH 3, the degree of purification of metal ions by adsorption was small (55-65%) and at pH 6, the adsorption was effective.

Table 4. Effect of contact time and pH on the adsorption of Ni(II) on the clays (Volume = 25 mL and [adsorbent] = 1 g/L.

Adsorbent	Timeofadsorption (h)	pH	[Ni (II)], mg/L·25
Zhetisaynaturalclay	0	3	50
	0.25		29,75
	0.5		32,75
	1		30
	2		30,75
	4		27,25
	6		30,25
	8		29
$MnFe_2O_4$/ Zhetisay	0	3	50
	0.25		46,5
	0.5		33,5
	1		37,25
	2		34,25
	4		29
	6		23,5
	8		28,5
$MnFe_2O_4$/ Zhetisay	0	6	50
	0.25		15
	0.5		11,5
	1		12,75
	2		12,25
	4		8
	6		9,5
	8		6,25

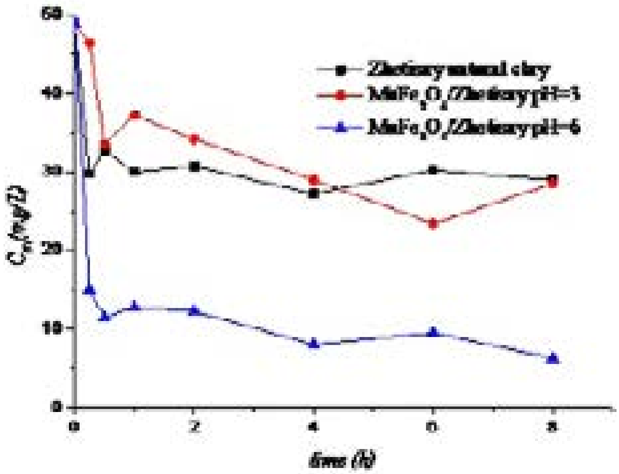


Figure 7. Effect of contact time and of pH on the removal of Ni (II) by adsorption with the Zhetisay natural clay and with the $MnFe_2O_4$/Zhetisay PILC (Operating conditions: initial concentration of Ni (II) = 50 mg/L, 2.5 g/L of adsorbent).

Conclusions. A method for obtaining $MnFe_2O_4$/clay composites with iron particles characterized by high magnetic properties has been developed. Studies of the elemental composition and the XRD determination method have established that the content of magnetite in the composites is determined by the cation exchange capacity of the adsorbent to iron ions, which is due to the chemisorption process.

It is shown that the use of composites containing Fe_3O_4 makes possible to obtain materials with pronounced magnetic properties at a low iron content, which is explained by the presence of particles.The introduction of magnetite particles into the structure of the natural clay leads to a decrease in the stability of the hydro-suspensions of composites and to a decrease in the size of the composites, which is due to an increase in the density of clay particles and to a decrease in their swelling when magnetite is introduced.

The synthesis and application of $MnFe_2O_4$/Zhetisay clay in water and wastewater treatment have been well studied and have been used in various ways to control water containing the heavymetal Ni(II). The research work showed that the inclusion of functional MNPs in clay structures led to the production of stable adsorbents that have increased recoverability and stability during processing. The adsorption capacity is related to the pH of the solution, pH = 6 is better than 3.

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