RESEARCH ARTICLE

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Decontamination of Soil with Natural Sorbents Bentonite

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ABSTRACT: As it is known, the main sources of pollution that have a great impact on natural geosystems are anthropogenic (industry, transport, energy, various wastes, etc.) and natural (volcanic eruptions, fires, various kinds of waves, etc.) factors. But despite this, targeted comprehensive studies of the impact of pollutants from enterprises of the transport complex, including railway, on the environment, both at the regional and national levels, have not been fully studied. The research study describes the physical and chemical properties of bentonite clay from the Urangai deposit in the South Kazakhstan region. We have conducted several experimental studies and collected materials on the characteristics of the Urangai bentonite clay deposit in the Turkestan region, which was previously given insufficient attention and which has not yet found widespread practical use, although it was explored in 1972, the volume of bentonite clay is about 6.8 million m^3. Clay reserves in this area are estimated at at least one million cubic meters.

Keywords: Bentonite, Sorbent, Clay, Urangai deposit, Kazakhstan.

INTRODUCTION

To create a stable balance of natural ecosystems, increase biological productivity, and preserve the species diversity of the gene pool of flora and fauna, including humans, in the coming future it is necessary not only to prevent pollution of the natural environment but it should also be considered that one of the most important tasks of the problem of environmental protection is inactivation, i.e. reducing the toxicity of potentially dangerous pollutants (heavy metals, pesticides and others) that are not subject to removal from biosphere objects, especially from soils, due to the course of natural self-cleaning processes (Tulepova et al., 2002; Alinia-Ahandani et al., 2019; Hajipuor et al., 2023). Therefore, in solving several environmental problems, the use of the possibilities of natural resources themselves, such as bentonite, i.e. its physico-chemical and other properties, represents a certain prospect.

Knowledge of the patterns of transformation, migration, accumulation, and translocation of pollutants in biosphere objects is fundamental, since based on them, by establishing the mechanisms of ongoing processes, it is possible to regulate the behavior of potentially dangerous heavy metals (HMs) and other ecotoxicants in specific natural environments, to develop new effective measures or technologies to ensure environmental management and environmental safety. Also, a certain perspective and relevance in solving several environmental problems is the use of the possibilities of natural resources themselves, i.e., clarifying the role of individual mineral and organic components in the processes of transformation and fixation of HM by soils, in their migration into the most important agricultural and industrial crops (Kozhamberdiev and Savinova, 2002; Alinia-Ahandani et al., 2019; Selamoglu et al., 2023). For example, the use of adsorbing, complexing, and catalytic properties of bentonite clay and its mixture with humic substances to solve specific environmental problems.

In the Republic of Kazakhstan, with its vast territory and significant needs, soil plays a primary role. The leading position in the agriculture of the Kazakhstan system is occupied by a healthy and fertile land area, but due to improper exploitation, it is exposed to various kinds of negative impacts. This already indicates that the area of land being withdrawn from agricultural use is growing every year. Considering the possibilities and prospects for improving the ecological state of the soil system in the Republic of Kazakhstan, we conducted scientific research on the example of the Urangai bentonite clay deposit. Based on experiments and analyses, the prospects of replacing chemicals and natural material bentonite are shown.

However, previously available developments aimed at reducing the toxicity of chemicals in the soil are either insufficiently effective or have not been brought to the level of regulatory indicators. In this regard, it is advisable to use an unconventional approach to solve existing problems, search for new and more advanced technologies, as well as create scientific foundations for environmental protection and environmental management (Savinova et al., 2002; Sunakbaeva et al., 2009; Sheydaei et al., 2020; Selamoglu et al., 2022).

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This work, aimed at developing theoretical foundations for creating effective methods of wastewater treatment, soil detoxification, and exhaust gas purification of diesel locomotives based on the use of natural materials and waste from agriculture and other industries, is relevant.

MATERIALS AND METHODS

The use of bentonite clay from the Urangai deposit in agriculture and the development of environmentally appropriate methods to reduce harmful effects on the soil system.

To achieve this goal, the following main tasks were solved:

- assessment of the role of bentonite clays in the processes of transformation, migration, accumulation, translocation of toxicants, and development of methods for managing these processes based on their established mechanisms;

- study of the structure and composition of bentonite from the Urangai deposit;

- development of a method for using a natural sorbent, that is bentonite in the process of soil neutralization.

The main idea is to use bentonite both in agriculture as a top dressing and in the process of detoxification of the soil.

In this regard, to identify the possibility of using a natural sorbent–bentonite clay of the Urangai deposit in various environmental technologies, for example, for soil detoxification and wastewater treatment, we conducted studies on the chemistry of its surface, colloidal chemical, adsorption-structural, ion exchange, complexing and other properties (Espembetov, 2005; Sunakbaeva, 2009; Hajipour et al., 2023).

As is known, the theoretical basis for explaining the migration of substances in nature, as well as for rational selection when using any natural sorbent in the processes of water purification, gas emissions, and other wastes are their physicochemical characteristics. The intensity and strength of adsorption interactions depend on these properties.

Based on the conducted analytical studies, the following component content (in %) was found in the selected clay: SiO2 – 55.72; $Al_2O_3 + TiO_2$ – 13.60; Fe_2O_3 – 4.63; FeO – 0.66; CaO – 2.94; MgO – 2.43; $K_2O + Na_2O$ – 3.65; humus – 1.54; hygroscopic moisture – 5.04. The SO42 content varies between 0.98% - 3.05%, which indicates the presence of gypsum, loss during calcination – 8.91%. In this clay, in addition to gypsum veins, there are also strong hardened layers of rocks that are easily separated from the clay.

The study of the physicochemical properties of bentonite clay. The extracted bentonite clays of the Urangay deposits contain from 65 to 87% dioctahedral montmorillonite, in the exchange complex of which calcium and magnesium cations predominate. The content of exchange cations averages 70 mg-eq/100g.

RESULTS AND DISCUSSION

Bentonite in the wet state is activated by soda ash, while calcium and magnesium cations are replaced by sodium cations, after which the properties of bentonite approach those of natural sodium bentonite of the currently known methods for determining the mineralogical composition of the clay fraction, the most reliable is the method of X-ray diffraction analysis, which allows obtaining both qualitative and quantitative characteristics of bentonite. Since bentonite was a monomineral composition, the mineralogical characteristic of the rock was obtained by optical method in transparent sections (Figure 1).

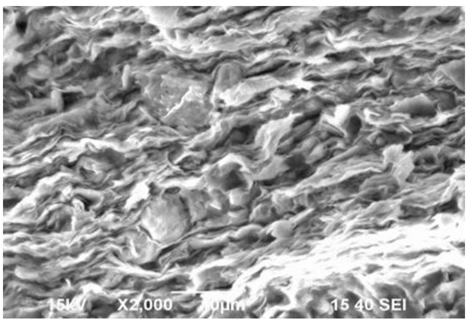

Figure 1. *Bentonite in transparent media*

However, this assessment is qualitative, very approximate, and can only be used to isolate rock sections to determine their mineralogical composition by X-ray diffraction. Based on the petrographic description, the full detailed name of the rock is given, including its structural appearance and material composition, and a brief conclusion about the genesis is given (Figure 2 and Figure 3).

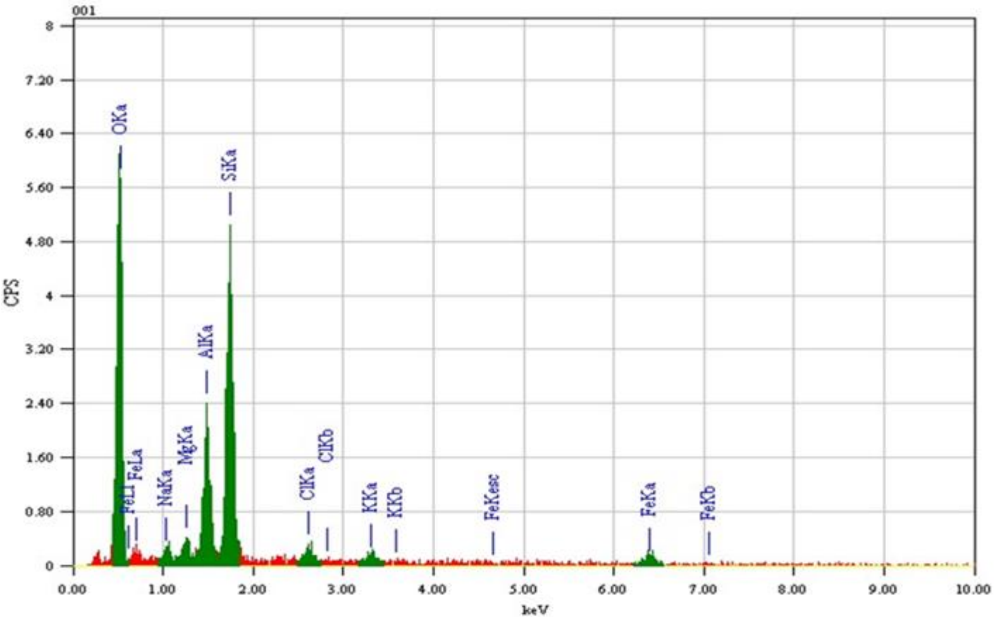

Figure 2. *Structural appearance and material composition*

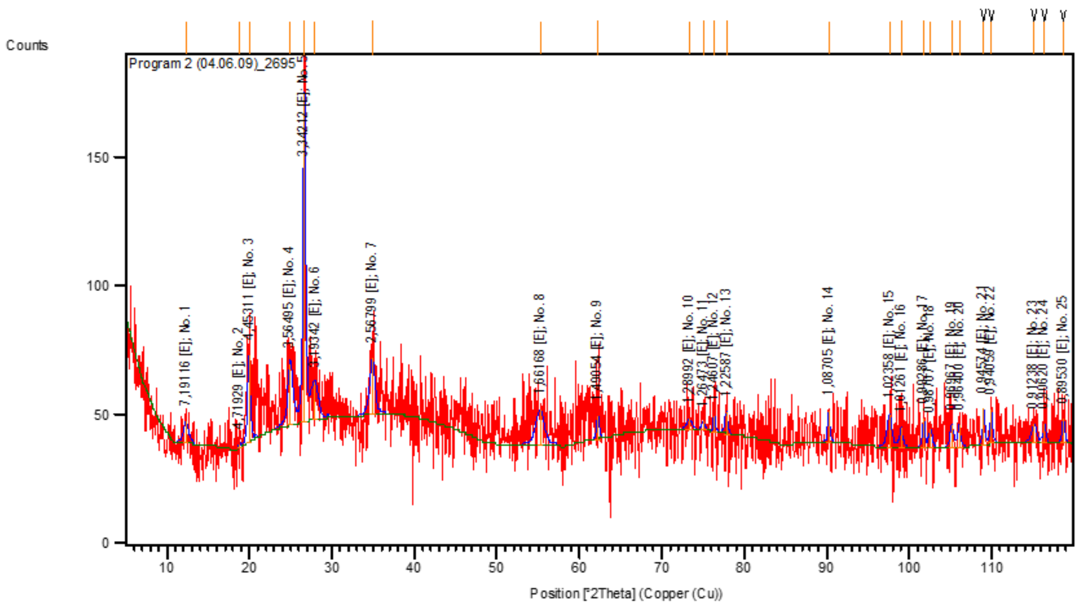

Figure 3. *A brief conclusion about the genesis*

The bulk in its natural composition is 594 kg/m3, and water absorption within 1 hour is 11%. Because the fixation and release of HM depend on the granulometric composition of the soil and clay material, respectively, and their transition from soil to plants, we conducted studies to determine it. The granulometric composition of the clay under study is as follows:

Fraction content in % of dry weight

mm:	0.5-0.05	0.05-0.01	0.01-0.005	0.005-0.001	less than 0.001
	10.7	15.2	12.3	34.0	27.8

From the data obtained, it can be seen that the content of the clay fraction (less than 0.005 mm) in the studied Urangai bentonite is 61.8%, i.e. two fractions prevail in the mechanical composition: silt and fine dust. The share of medium and coarse dust accounts for 12.3 and 15.2%, respectively, and the content of medium sand (0.5-0.25 mm) is 10.7%.

Since the quality of clay materials is also determined by their physical properties, we have established the volume weight, true and apparent specific gravity, and porosity (Table 1).

Table 1. *Physical properties of bentonite clay of Urangai deposits*

Laboratory number	Volumetric weight, g /cm^3	Specific gravity, g /cm^3		Porosity	
		true	apparent	%	cm^3 /g
1	1.180	2.5921	1.350	46	0.321
2	1.176	2.6013	1.350	47	0.300
3	1.159	2.6442	1.491	45	0.295
4	1.120	2.7029	1.522	43	0.280
5	1.180	2.6167	1.509	44	0.315

Porosity was determined because the ratio of the number of large (macropores, pore sizes >50 nm) and small pores (micropores, pore sizes <2 nm) depends on the actual adsorption capacity of the dispersed material. In turn, the porosity of naturally dispersed bentonite should be determined by the structural feature of the mineral included in its composition, the quantitative and mineralogical composition, the conditions of formation of the deposit, and the composition of the exchange complex (Kolupaeva et al., 2009; Riaz et al., 2023; Hajipour et al., 2023).

Some experimental data obtained by us in the study of the properties and composition of bentonite clay are presented in Tables 2 and 3.

The studied bentonite has high plasticity, as well as high dispersion, which determines its developed outer surface. The specific surface area of this bentonite clay is on average 125 m^2 /g.

Table 2. *The specific surface area of Urangai bentonite clay (S) and the maximum sorption volume (Vs).*

Laboratory numbers	S, m^3 /g	V_s, cm^3 /g	Exchange complex, mg – eq/100 g of clay			
			Na^+	Ca^{2+}	Mg^{2+}	$\sum$
1	78	0.17	48	33	9	80
2	120	0.22	50	41	8	100
3	69	0.16	32	25	6	63
4	132	0.25	54	33	6	93
5	130	0.25	39	32	7	78

Table 3. *Composition of the aqueous extract of Urangai bentonite, %.*

Laboratory sample numbers	Dry residue	HCO_3	Cl^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	Na^++K^+
1	5.280	0.120	2.090	0.482	0.148	0.020	2.982
2	5.101	0.115	2.120	0.490	0.130	0.038	3.108
3	5.238	0.094	2.156	0.478	0.140	0.030	1.980
4	4.998	0.102	2.108	0.485	0.150	0.041	2.795
5	5.644	0.089	2.110	0.500	0.162	0.022	3.020

As can be seen from Table 3, the aqueous extract of Urangai bentonite clay contains mainly chlorides and sulfates.

The absorption capacity of exchange cations for Urangai bentonite ranges from 63-100 mg-eq/100 g, pH =7.5-7.7 (aqueous) and pH=7.0-6.8 (saline).

A sufficiently high capacity of cation exchange indicates the possibility of creating conditions for the retention of HM by introducing bentonite clay into soils, which will reduce their availability to plants and living organisms.

As a result of mineralogical analysis, it was revealed that bentonite clay of the Urangai deposit mainly represents a genetic mixture of montmorillonite (65-75%) and hydrolysis, muscovite, biotite, kaolinite (no more than 5%) are found in small quantities in the form of impurities. The main mineral in bentonite clay has a dioctahedral structure, is three-layered, i.e. in its lattice, two tetrahedral silicon-oxygen layers account for one aluminum-oxygen-hydroxyl octahedral layer. There is a large space between the layers in the mineral, so when using them as a sorbent, the adsorbed substances can penetrate into it. The interplane distance usually increases with hydration or under the action of low molecular weight organic substances.

Chemical activation of bentonite clay was carried out during the day by treatment with sulfuric acid solutions of various concentrations. Washed with distilled water and dried clay is used to establish its adsorption activity and determine its chemical composition.

An increase in the content of silicon oxide from 55.72 to 66.3% and a decrease in one-and-a-half oxides from 18.9 to 10.2% was found, which is explained by the transition of silicon to an acidic form and the leaching of aluminum and iron oxides from the crystal lattice of the mineral (Sunakbayeva et al., 2008; Kolushpayeva et al., 2009; Ahandani et al., 2022).

The data characterizing the structural and sorption properties of bentonite clay after treatment with sulfuric acid are presented in Table 4.

Table 4. *Structural and sorption properties of Urangai bentonite after activation with sulfuric acid during the day*

Acid concentration, %	Bulk weight powder, g/cm	Specific gravity g/cm^3		Total Porosity (P), %	Total pore volume (V∑) cm^3/g	Static activity (Vs), cm^3/g	
		true (d)	apparent (δ)			By water	for benzene
-	1.180	2.644	1.521	45.5	0.30	0.16	0.14
5	0.845	2.622	1.483	46.0	0.37	0.44	0.24
10.0	0.762	2.596	1.33	55.2	0.48	0.34	0.32
20.0	0.654	2.358	1.04	63.7	0.80	0.31	0.36
25.0	0.631	2.255	0.88	67.5	0.93	0.33	0.45
30.0	0.627	2.104	0.77	69.4	0.98	0.28	0.62

Based on experimental data, an increase in the sorption capacity of the clay in question was revealed, which is expressed in an increase in total porosity, total pore volume, and an increase in static activity in water and benzene, respectively, by 2 and more than 3 times (at a concentration of sulfuric acid - 25%).

The analysis of the obtained results shows a change in the porosity of clay, which is apparently due to the destruction of the crystal lattice, as is known from the literature /1-2/, due to the leaching of aluminum oxides, silicon, magnesium, calcium, iron, etc., etc. Upon activation, as can be seen from the data given in Table 4, the specific surface area increases from 78-132 m^2/g to 112-180 m^2/g, the maximum adsorption volume increases more than 3 times, the volume of transient and micropores, which are respectively determined by the absorption of water vapor and benzene and it is on their volume that the adsorption process depends. The volume of micropores is not lower than 0.05 cm3/g, and transitional ones are not lower than 0.25 cm^3/g.

In our studied bentonite, montmorillonite is the main rock-forming mineral, it is a layered silicate with an expanding structural cell. During the adsorption process, one or more monomolecular layers of the adsorbed substance are introduced into the inter-pack space, as a result of which the size of the micropore changes. The results show better water adsorption compared to nonpolar benzene. As is known from physical chemistry, like dissolves in like, i.e. this indicates the hydrophilicity of the clay surface.

The hydrophilicity of bentonite clay is due to both the structural feature of the montmorillonite mineral with an expanding crystal lattice (2:1 structure) and its high dispersion. In addition to the outer surface, Montmorillonite also has an inner surface, which manifests itself when the layers of the crystal lattice expand during the filling of the interlayer space with polar water molecules. In addition to water molecules, molecules of other polar compounds – ammonia, alcohols, amines, etc. - can penetrate the interlayer (interlayer) space of montmorillonite. The fraction content of less than 0.005 mm in this bentonite clay is on average more than 60%, in it the colloidal fraction (<0.2-0.3 microns) is about 50-85%, and swelling (volume increase) is 12-17 times.

Studying the patterns of accumulation, transformation, and translocation of heavy metals in the soil-plant system

The soil, being at the intersection of all transport routes of migration of toxicants, acts as a regulator of global cyclic processes of mass transfer of chemical elements and energy, as the most sensitive indicator characterizing the ecological situation in the landscape. The high sensitivity and vulnerability of the soil cover are due to the limited buffering and resistance of soils to the effects of forces that are not peculiar to it in an ecological sense. In this regard, the assessment of the danger of contamination of the soil system is carried out by taking into account that it is buffering since migration, accumulation, and translocation of ecotoxicants depend on it. The main components that create buffering include fine mineral particles, humus, pH values of the medium, and redox properties.

The effect of man-made effects on the physico-chemical properties of soils. As is known, the main components polluting the atmospheric air, which account for about 88% of all emissions, are man-made dust, including mineral and organic compounds of heavy metals and other elements, as well as carbon, nitrogen sulfur oxides, and hydrocarbons. And between the surface layer of atmospheric air and the surface layer of soil, there are always continuous interrelated processes – the deposition of pollutants from the air to the soil surface and, conversely, the rising of dust particles from the soil surface into the air basin. Therefore, the content of pollutants, in our case, the content of HM, in the surface soil layer can serve as an indicator of soil contamination, and the content of HM in fine soil fractions is an indirect indicator of their content in the dust of the surface layer of atmospheric air.

To study the effect of man-made effects on the acidity of the environment and the redox properties of soils, a series of model experiments were conducted. Oxides and salts of HM and arsenic were used as pollutants, while their concentration varied between 1-100 maximum permissible concentration (MPC) (Table 5).

Table 5. *Change in the pH of serozems during the introduction of HM compounds.*

The number of deposited trademarks heavy metals	The pH of the soil solution (numerator) and rH2 (denominator) when applying the following HM compounds			
	Nitrate	Sulfate	Chloride	Oxide
		Copper		
Control	7.3/31.2	7.3/31.2	7.3/31.2	7.3/31.2
1 MPC	7.2/31.5	7.0/32.4	7.0/32.3	7.3/31.0
10 MPC	7.0/31.8	6.6/33.1	6.7/33.0	7.0/31.7
50 MPC	6.9/31.6	5.1/33.5	5.0/32.6	7.0/31.5
100 MPC	6.5/32.3	4.3/33.7	4.5/29.7	7.0/32.5
		Zinc		
Control	7.2/29.4	7.2/30.1	7.2/28.9	7.2/30.1
1 MPC	7.2/29.9	7.0/30.2	7.1/29.0	7.2/30.1
10 MPC	7.1/30.4	6.9/30.1	6.8/28.4	7.2/30.2
50 MPC	7.0/30.3	6.6/31.4	6.5/30.1	7.2/30.2
100 MPC	6.8/30.4	6.4/30.9	6.2/30.3	7.2/30.2
		Lead		
Control	7.3/29.4	7.3/29.4	7.3/30.2	7.3/30.0
1 MPC	7.3/30.0	7.3/29.3	7.2/30.2	7.2/29.9
10 MPC	7.1/30.0	7.3/29.4	7.0/30.8	7.2/30.1
50 MPC	7.1/30.2	7.3/29.1	7.0/30.9	7.4/29.7
100 MPC	7.0/30.5	7.3/29.3	7.1/31.1	7.3/29.7

Management of the translocation of heavy metals using bentonite. The search and development of effective methods that make it possible to obtain clean crop products from technogenically polluted soils is an urgent task for the agro-industrial complex (Sunakbayeva et al., 2008; Alinia-Ahandani et al., 2019). To transfer HM from a mobile form to a stationary one, several studies have been carried out to fix them in the soil system by creating a geochemical barrier using bentonite clay and its mixture with humic acid (HA), rice, and wheat waste with high sorption activity (Table 6). Contamination with large amounts of HM was carried out by artificially introducing them into the soil.

Table 6. *The content of heavy metals in the studied objects, mg/kg.*

The name of the object under study	Metal content, mg/kg				
	without adding sorbents		in plants when applying sorbents		
	in soils of the gray-earth	bentonite and rice waste is serozem	bentonite serozem	bentonite and GC serozem	bentonite and wheat waste is serozem
			Lead		
Corn	60.2/77.8	16.4/0.5	1.4/0.2	0.4/0.2	not defined
Corn	150.5/168.1	69.1/1.3	0.6/0.5	0.6/0.4	0.1/0,03
Corn	200.5/218.1	72.6/1.3	0.6/0.4	0.7/0.4	0.2/not defined
Corn	500.2/518.4	80.3/1.1	1.2/0.4	0.8/0.3	0.3/not defined
			Copper		
Corn	100.0/120.5	20.5/19.1	16.6/15.7	9.8/15.2	0.3/0.2
Corn	250.0/270.6	22.8/19.2	9.1/6.8	5.9/6.6	0.2/0.2
			Zinc		
Corn	120.2/125.0	6.9/4.7	6.1/3.9	5.1/3.7	4.1/2.8
Corn	300.0/312.2	7.7/4.9	6.9/2.7	5.5/2.7	3.7/1.6

As follows from the experimental data, as a result of introducing a mixture of bentonite with HA, rice, and wheat waste into the soil, the amount of HM entering the studied corn crop did not exceed regulatory levels even on heavily polluted soil (permissible levels in forage plants of lead – 0.5 mg/kg, cadmium – 0.1 mg/kg, zinc – 50 mg/kg, copper – 10.0 mg/kg).

Thus, based on model experiments, the possibility of transferring HM to a firmly fixed state due to the adsorption properties of the considered mixture of natural materials has been revealed.

Based on the analysis of literature data and experimental studies of the complex properties of bentonite clay of the Urangai deposit of the Turkestan region and its mixture with humic acid, rice, and wheat waste, the features of their structure, composition, basic physicochemical and other properties are established, their quality and characteristics are assessed. The sorption properties of these mixtures with respect to heavy metals and other ecotoxicants have been studied and the role of mixtures and each component separately in the processes of translocation, migration, and accumulation of heavy metals in the soil and the soil-plant system has been determined.

The bentonite clay of the Urangai deposit studied by us is a chemically inert substance with low alkalinity. It has good swelling and high colloidality, as well as ion-exchange properties, which indicates the possibility of their use for the extraction of metal and nonmetal ions from aqueous and other media.

Based on the revealed patterns, it has been established that the acidity of the soil solution, the content of clay minerals, and the nature and composition of humic substances play a decisive role in protecting plants from the damaging effects of excessive concentrations of TM. These results were used to control the processes of migration, accumulation, and translocation of heavy metals in the soil system and in the soil-plant system.

Based on the establishment of physico-chemical, adsorption-structural, ion-exchange, and other properties of natural bentonite clay from the Urangai deposit, the scientific basis for its use in soil detoxification processes has been developed. The possibility of using a mixture of bentonite with humic acid or with agricultural waste for the detoxification of soils from heavy metals is shown.

CONCLUSION

The main sources of pollution that have a great impact on natural geosystems are anthropogenic (industry, transport, energy, various wastes, etc.) and natural (volcanic eruptions, fires, various types of waves, etc.) factors. Based on the revealed patterns, it has been determined that the acidity of the soil solution, the content of clay minerals, and the nature and composition of humic substances play a decisive role in protecting plants from the destructive effects of excessive TM concentrations. Our research study characterizes the physical and chemical properties of bentonite clay from the Urangai deposit in the South Kazakhstan region. These results were used to control the processes of migration, accumulation and transport of heavy metals in the soil system and in the soil-plant system.

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CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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