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Experimental Studies on Wastewater Sorption Treatment with Subsequent Disposal of Used Sorbents

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The research proposes the method for cleaning of the chromium-containing wastewater by the modified sorbents based on the natural aluminosilicates of East Kazakhstan deposits, local wood waste and fibrous materials that differ by cheap, good sorption properties, availability and security in the environmental terms.
The research of the waste complex sorbents for utilization in one of the most resource-intensive industries - the construction industry - is highly relevant and promising to create the necessary preconditions for the industrial development of the construction binders for various technology areas. The application of the research results will make sound recommendations how to expand the resource base, to use industrial raw materials in the production process, and to reduce the cost of widely used materials and products in the construction practice. The important factor in the technical and economic term is that the residue from the treated waste water is environmentally friendly since the chromium ions and other heavy metals have the form of the complex compounds. The complex compounds are environmentally safe and can be recycled in various building materials. The optimal construction materials for the utilization of the waste sorbents are mortar and concrete.

1. Introduction

Industrial wastewater polluted surface and groundwater widespread, it is leads to environmental degradation. Surface and groundwater pollution in industrialized regions issue is especially acute. The problem of pollution by toxic heavy metals is relevant for many countries in the world. Therefore, primary and great importance has studies carried out to improve the ecological state using accessible and environmentally friendly technologies and materials.
Currently, in East Kazakhstan region, where large industrial enterprises are concentrated, there is a negative impact of the complex of different industries on the environment, including surface and ground water which is contaminated, particularly, by chromium-containing compounds. Traditional methods of wastewater treatment do not allow deep purification of such wastewater, therefore effective and environmentally beneficial methods of wastewater purification are constantly being sought (Marrugo et al., 2015).
There are many methods of purification from chromium-containing wastewater, but the most common and effective methods are sorption ones (Bougdah et al., 2017). The efficiency of the adsorption purification reaches 80 – 95 % and depends on the chemical nature of the adsorbent, its structure and size of the adsorption surface. Recently the great importance is given to natural sorbents (Bhattacharyya et al., 2008).
Natural sorbents - bentonite clays possess pronounced sorption properties (Balintova et al., 2016). In addition, the economic effect of the use of natural sorbents is achieved by sufficiently close proximity of the deposits of these materials to the consumer, what ensures low transport costs and does not have significant effect on the cost of production.
East Kazakhstan region has significant reserves of natural aluminum silicates. Bentonite clay of Tagansk deposit occupies a special place among the natural clay sorbents (Kravchenko et al., 1996).
Also, materials obtained from the wastes of various industries such as woodworking industry, grain processing industry, textile industry and others can be used to replace traditional sorbents (Kadirvelu et al., 2001).

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However, the use of these materials in pure form as sorbents is ineffective, so they need to be exposed to different ways of activation. To make the properties of the bentonite clay more specific and give specific sorption activity scientists carry out its modification. The developed modified sorbents should have high sorption capacity and sorption properties. They have to become so competitive as the AS and MS analogues of Alsis, BIRM, EcoSoft, Purolite, Greensand companies and others.
It is known, that the sorption properties of the clay can be significantly altered by chemical modification. Thereby, the study of the modification of the clay properties deserves great attention. The important studies on the effect of chemical modification on the sorption properties of solids were carried by Bougdah et al. (2017) .

2 The waste water sorption purification research

In our research, the modification process consisted in the preliminary thermal activation of the bentonite clays and the sawdust reagent activation, and then mixing obtained components. To form the modified sorbent, bentonite clays of Tagansky deposit 14th horizon of East Kazakhstan and different ratios pine sawdust of local origin compositions based were made.
Bentonite clays and pine sawdust were grinding by mill knife with subsequent sieving. Sorbents - bentonite clays, 0.1 mm in diameter, were thermally activated in an electric furnace at 300 °C for 1 h.
We have performed experimental studies of chromium ions sorption for 3 and 6 h at the initial concentration 100 mg/dm^3 with the use of complex sorbents activated by sulfuric acid (1, 5, 10, 15 %), hydrochloric acid (5, 10 %), and sodium carbonate (5, 10 %). After sorption purification, the precipitate was filtered through a "white tape" filter. The residual content of chromium ions in solutions was determined by the atomic-absorption method by using mass spectrometer with inductively coupled plasma ICP-MSAgilent 5700 cx from Agilent Technologies (USA).
The extraction rate was calculated by analysis results:

$$\alpha = \frac{C_0 - C}{C_0} \times 100\ \% \qquad (1)$$

where, C_o- original content component in solution, mg / dm^3;
C - is the residual component concentration in solution, mg / dm^3.
Compared with other types of modification only activation of complex sorbents by 10 % sodium carbonate solution has showed good results in purification - 99.65 % at the S: L ratio of 1:10 and the processing time equal to 24 h.
We obtained mechanically activated modified sorbents of several compositions to reduce the consumption of bentonite clays in relation with fibrous materials and to reduce bentonite clays based sorbent preparation time with sorption capacity saving.
To the mechanical components activation was used a vibratory mill, in which the material is crushed by hitting and abrasion. Steel rollers used as grinding bodies. The vibrating mill construction, in comparison with the rotary type ball mills, provides intensification of the process in 5 -10 times and carry out wet grinding process allows (Daumova et al., 2015). Studies on the chromium ions sorption purification with the use of mechanically activated complex sorbents based on bentonite clay and pine sawdust have shown the following results (Table 1).

Table 1: The results of wastewater treatment from chromium ions by complex sorbents at the initial concentration C_{oCr}= 0.034 mg/dm^3

Types of modified sorbents	Treatment time, h	S: L ratio					
		1:50		1:100		1:130	
		C_{Cr}^{3+}, mg/dm^3	α, %	C_{Cr}^{3+}, mg/dm^3	α, %	C_{Cr}^{3+}, mg/dm^3	α, %
bentonite clay:	3	0.0004	98.82	0.0009	97.35	0.00090	97.35
sawdust (2:1)	6	0.0039	82.27	0.001	95.45	0.00087	97.44

Our studies have shown high efficiency of water treatment by the complex sorbents obtained on the basis of bentonite clay and pine sawdust at the ratio of sorbent: chromium-containing wastewater (S: L) 1: 130.
So, to increase the efficiency of sorption the use of bentonite clays and basalt fibres is proposed.
In our studies as a raw material the bentonite clay is used. It is the bentonite clay of 14 horizon of Tagansk deposit with the basalt fibre.

In order to change some of the technological parameters several pasty sorbents of some compositions are obtained by the method of mechanical activation. Table 2 shows the results of the research on the wastewater treatment of reinforcing plant of Ust-Kamenogorsk by the sorbents based on the bentonite clay and the basalt fibres. We investigated the relation of the bentonite clay and the basalt fibres in the ratio of 2:1.

Table 2: The results of wastewater treatment of Ust-Kamenogorsk reinforcing plant from chromium ions by the complex sorbents based on the bentonite clay and the basalt fibres at the initial concentration C_{oCr} = 0.034 mg/dm^3

Types of modified sorbents	Treatment time, h	S: L ratio					
		1:50		1:100		1:130	
		C_{Cr}^{3+}, mg/dm^3	α, %	C_{Cr}^{3+}, mg/dm^3	α, %	C_{Cr}^{3+}, mg/dm^3	α, %
bentonite clay : basalt fiber (2:1)	3	0.0008	97.65	0.0007	97.94	0.001	97.06
	6	0.0032	85.45	0.004	81.81	0.0015	95.59

It should be noted that the studies have shown high efficiency of wastewater treatment by the sorbents obtained on the basis of bentonite clay and fibrous materials in all proportions of the sorbent to chromium-containing wastewater.

3 Used sorbents utilization studying as an additive to building materials

The waste bentonite sorbent is supposed to utilize in one of the most resource-intensive industries - the construction industry. In our view, to use the waste sorbents in mortars is the optimal variant. In our studies cement “Heidelberg Cement PC 400 D20” of Bukhtarma cement company is used as a binder. The actual activity of the cement has been determined by the standard method and amounted to 430 kg / cm^2. Sand of the enterprise "The Plant of Nonmetallic Materials" of Ust-Kamenogorsk was used as the filler, which relevant GOST is 8736, fineness modulus Mk is 2.69, true density is 2.63 g/cm^3, bulk density is 1,581 kg/m^3, emptiness is 40 %.

The modified waste sorbents are used as the fillers. The determination of the influence of the waste sorbents additive by identification of the optimal dose was solved in the research of physical and mechanical properties of mortars. The pattern composition of the mortar is adopted. It is the cement and sand mortar in the ratio of 1: 3. The waste sorbent additive is introduced in the amount of 2, 5 and 10 % by weight of the cement.

All samples of the homogeneous mortar have been tested for strength at the predetermined age according to GOST 10180-90. The research results are presented in Figures 1 and 2.

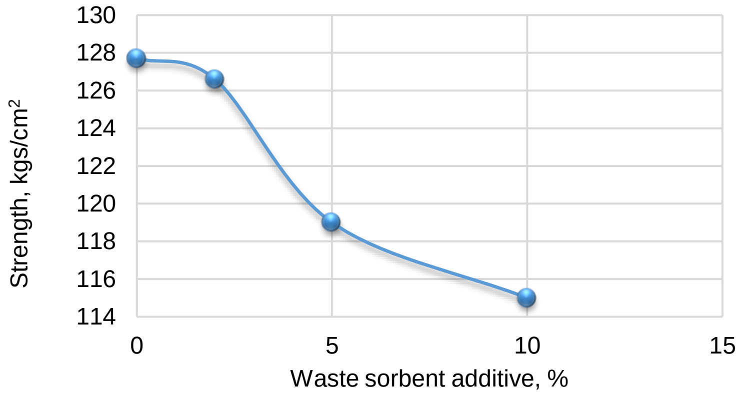

Figure 1: The effect of waste sorbent (bentonite and sawdust) on the strength of the mortar

Figure 1 shows the results of the effect of waste sorbent additive containing activated sawdust on the strength of the mortar.

In Figure 1, there is a sharp drop in the strength of the solution. Presumably this is due to the effect of high alkaline liquid phase of the cement (pH = 12...14) on the structure of the sawdust. The effect of the alkali

produces leaching of wood and causes its significant decomposition, which might lead to the slowdown of the processes of hydrolysis and hydration of the cement.
The studies have shown that the greatest increase in the strength of the mortar is achieved with the introduction of the waste sorbent based on the bentonite and basalt fiber (Figure 2).

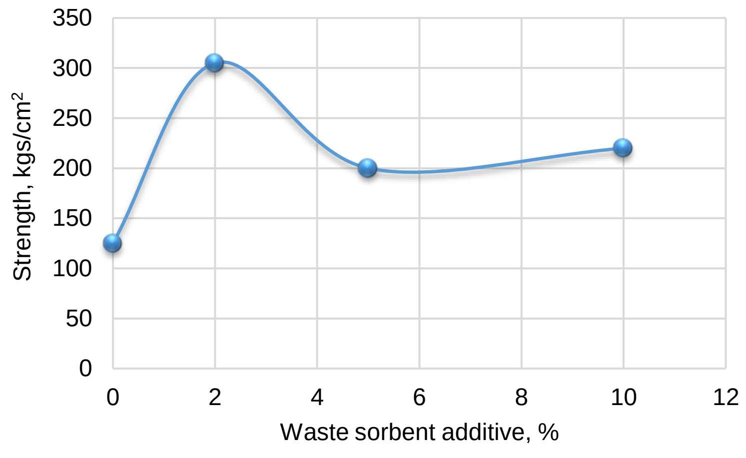

Figure 2: The effect of waste sorbent (bentonite and basalt fibre) on the strength of the mortar

Figure 3 shows the investigation results of the effect of the waste sorbent additive method on the strength of the mortar. The introduction of the additives in the amount of 2 – 5 % in the dry form into the cement and sand mixture increases the strength of the mortar samples by 30 %, and tempering water by 18.9 %. The further increase of the number of additives reduces the samples strength simultaneously in both cases.

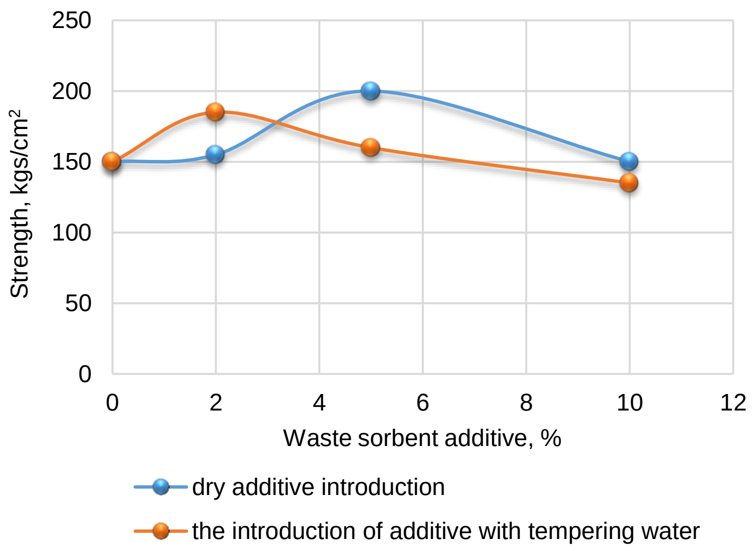

Figure 3: The effect of the method of the waste sorbent additive introduction on the strength of the mortar

The morphology of the cement composition has been also studied by scanning electron microscope JSM-6390LV at the laboratory of engineering profile "Irgetas" at D. Serikbayev East Kazakhstan State Technical University (Figures 4 and 5).

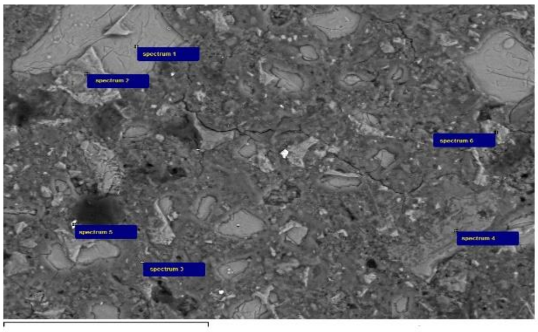

Figure 4: The morphology of the cement stone

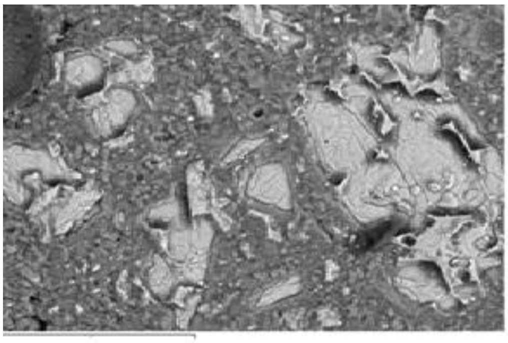

Figure 5: The morphology of the cement stone with waste sorbent additive, including bentonite and sawdust after activation by sodium carbonate

In the pattern free-additive sample of the cement stone the research (Figure 4) shows the presence of the dense plate and squamous new formations of calcium hydrosilicate and closely packed plate crystals of portlandite with well viewed cleavage planes. The fibrous crystals of ettringite are not detected. There is a small amount of crystals of low-sulphate form - calcium monosulfoaluminate. In some areas of the cement stone the clusters of relatively large cubic and hexagonal crystals belonging to calcium hydroaluminate and hydrogarnet are discovered. The overall structure of the micro-relief can be described as tight.
The different picture is presented in the cement stone, containing the waste sorbent additive. Portlantide crystals are not found. There are areas of the cement stone formed by new formations of calcium hydrosilicate (Figure 5). Figure 6 shows micrographs of the mortar filled with the waste sorbents containing sawdust.

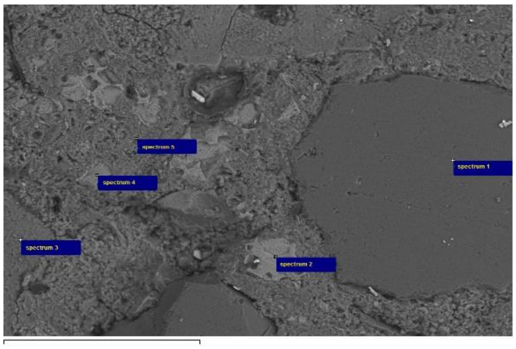

Figure 6: The mortar with the waste sorbent additive, comprising bentonite and sodium carbonate sawdust after activation

Figure 7 shows the composition of the mortar hardened by basalt fibre additive.

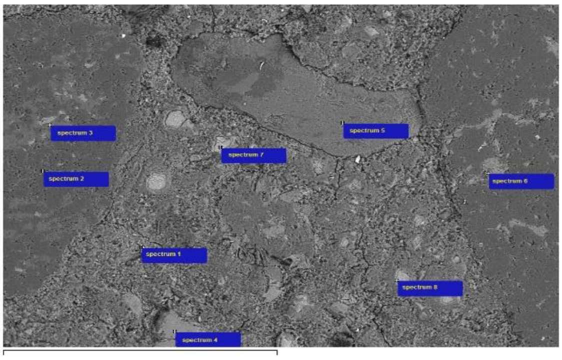

Figure 7: The mortar with the waste sorbent additive, including bentonite and basalt fibre

As a result of the introduction of the waste sorbents additive based on the bentonite and basalt fibres into the mortar the complex physical and chemical processes, resulting in the increased strength, water resistance, and frost-resistance of the material occurs. In this case the improving of physical and mechanical properties of the concrete occurs owing to many factors, the most important of which are: reducing of porosity by filling micropores and capillaries of matrix by new formations and dispersive basalt fibres.
Because of the opportunity to use waste sorbents in the building materials production it is necessary to explore the possibility of the environmental pollution by leachate products in the case of reaction with water. For this purpose, test specimens of mortar with the mentioned above additives were placed in the distilled water and after 5 weeks, the residual content of chromium ions were determined by atomic absorption method at the laboratory of engineering profile "Irgetas" of D. Serikbayev EKSTU. In the aqueous extract the presence of the chromium ion was not determined. The observed effect was connected to the fact that when the waste sorbents were mixed with the cement, chromium ions were bound by solid phase, and thus they resisted leaching. There was some sort of encapsulation of chromium ions in the solid matrix called the cement stone, which prevented chromium ions from the introduction into the aqueous extract.

4. Conclusions

The modified sorbents based on the bentonite clay, sawdust and basalt fibres show a high cleaning effect at the ratio of the sorbent to the chromium-containing liquid (S: L) 1 : 130, and the possibility of the reclamation of the spent sorbents of the various modifications in the production of the construction materials for various purposes with addition in the amount of 2 – 5 %. While using waste sorbents comprising bentonite and basalt fibre the amount of the admixture may increase up to 10 %.
Filling of the matrix of the cement composition by dispersed particles of the waste sorbent is one of the ways to improve the basic characteristics of the mortars. As it has been noted by several investigators, the addition of small amount of bentonite into mortars may thicken and strengthen its structure. This is due to the decrease of water separation by means of the increased water-holding capacity of bentonite clay, what is a consequence of the structural hydrargillite swelling of bentonite clay layer, the thin layer of mesh and fibre matrix of microfibers adsorbed on the surface by its contact with the tempering water. In this case water retained by bentonite particles provides all silicates and aluminates with the entry into the process of hydration, in consequence of which the cement stone is formed.
The important point in technical and economic terms is that the residue obtained after the purification of waste water is environmentally friendly, as chromium ions and other metals are in the form of complex compounds, which are safe for environment and can be utilized in a variety of building materials.

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