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Application of Modified Sorption Material for Efficient Wastewater Treatment of Galvanic Production[1]

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The galvanic production is one of the source of environmental contamination by harmful substances and especially heavy metals. The questions of water pollution prevention by wastewater containing heavy metal ions, are closely linked to the development of event to reduce fresh water consumption for technological needs of production and to reduce the amount of wastewater. One solution to this problem is the creation of low-waste and waste-free environmentally safe production processes of sewage treatment with the use of treated wastewater in the working cycle, which leads to a reduction of negative impacts on the environment.

Keywords: sorption detoxification, heavy metal ions, modified sorbent, dolomite rocks.

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Применение модифицированного сорбционного материала для эффективной очистки сточных вод гальванического производства

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Одним из источников загрязнения окружающей среды вредными веществами, в первую очередь тяжелыми металлами, являются гальванические производства. Вопросы предотвращения загрязнения водоемов сточными водами, содержащими ионы тяжелых металлов, тесно связаны с разработками мероприятий по сокращению потребления свежей воды на технологические нужды производства и уменьшению количества сбрасываемых стоков. Один из путей решения данной проблемы – создание малоотходных и безотходных экологически безопасных технологических процессов очистки сточных вод с использованием очищенных стоков в оборотном цикле, что приводит к снижению негативного воздействия на окружающую природную среду.

Ключевые слова: сорбционное обезвреживание, ионы тяжелых металлов, модифицированный сорбент, доломитовые породы.

The current state of the problem

A sorption extraction of metals is one of the most effective methods of using electroplating wastewater treatment; the efficacy of sorption purification is 80–95 % depending on the used sorbent. Sorption methods of wastewater treatment using the natural sorbents are acquainted for a long time, however, there is a large class of natural sorbents – minerals which due to the lack of knowledge is not widely used [16]. In the meantime, high sorptive properties, cheapness, abundance in nature make them cost-effective raw materials in technologies of treating industrial wastewater. The use of natural materials in wastewater treatment is acceptable from an environmental and economic point of view, but often such of materials do not have the desired sorptive properties, and they must be thermally modified. As a result of the modification, we obtain the sorbents which are different from the original mineral of natural surface which combine the useful properties of original material and the synthetic sorbents [7]. Therefore, the search of efficient and cost-effective natural sorbents for an intensification of wastewater treatment is an urgent problem [8, 9].

Research technique

We studied the sorptive method of heavy metal removal, as an example Cu (II); Ni (II) and Zn (II) from the aqueous solutions of a modified sorbent, based on the dolomite raw. This sorbent, Akdolit Kesselburger Pelm Gran CM3 (Akdolit-Gran) is produced in Germany and widely used in the West, and the European part of Russia.

The sorbent material passes the thermal modification by heat treatment of a mineral. A calcination promotes loosening the rocks to form a structure with greater porosity and specific surface [10, 11]. The approximate chemical composition of Akdolit-Gran are calcium carbonate, $CaCO_3$ – 68,9 %; calcium oxide CaO – 1,4 %; magnesium oxide MgO – 25,4 %; magnesium carbonate $MgCO_3$ – 0,6 %; iron oxide Fe_2O_3 – 0,6 %; alumina Al_2O_3 – 2,7 %; silicon oxide SiO_2 – 0,3 %; water H_2O – 2,7 %. The presented values are average for several years of regular testing.

Research results

The aim of research was to study the physicochemical and sorptive properties of Akdolit-Gran sorbent.

For carrying out the sorption process in the laboratory environment was used a method of alternating batches of sorbent and constant volume of the initial concentration of the solution: Cu (II) = 60 mg/dm^3; Ni (II) = 15 mg/dm^3; Zn (II) = 20 mg/dm^3. These concentrations are most common in wastewater of the electroplating. The residual concentration was determined by an atomic emission spectrometer with inductively coupled plasma, ICAP-6500. Mineralogical sorbent composition was determined based on X-ray diffraction analysis performed on DRON-3, in a Cu-Ka radiation, Fig. 1.

Analysis of diffraction patterns shows that the main phase in the sorbent is calcite $CaCo_3$ (d = 0.38; 0.30; 0.23; 0.19; 0.18 Å), in addition, there is a considerable amount of magnesium oxide MgO (d = 0.21; 0.15 Å). Diffraction peaks with the low intensity correspond to magnesium hydroxide Mg $(OH)_2$ (d = 0.21; 0.15 Å) and calcium hydroxide Ca $(OH)_2$ (d = 0.49; 0.26 Å), formed by hydrolysis of magnesium and calcium oxides contained in the sorbent.

The rest of the substances listed in the technical documentation for the sorbent ($MgCO_3$, Fe_2O_3, Al_2O_3, and SiO_3) have been identified because of their low concentration. The thermal analysis was conducted for a more detailed study of the sorbent sample with the help of STA 449 F1 instrument (simultaneous thermal analyzer), NETZSCH company (Germany) in an inert argon gas environment.

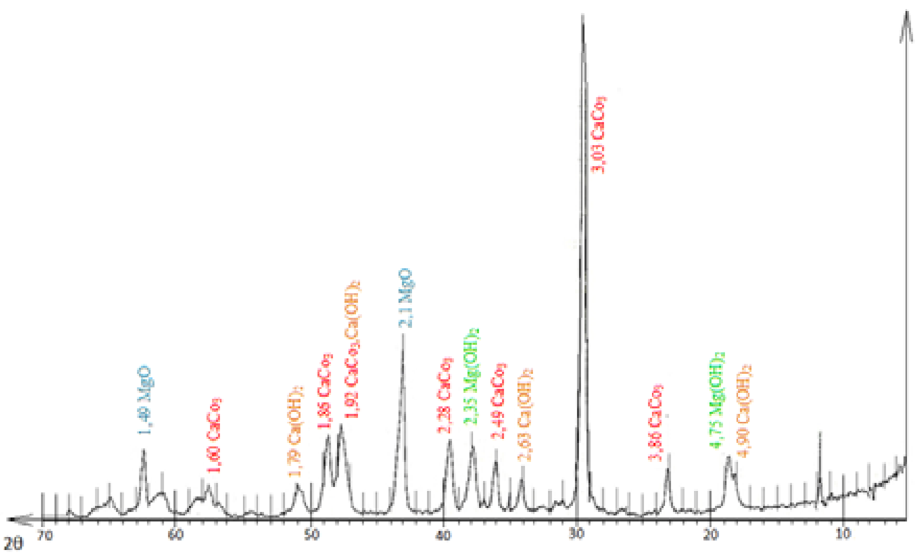

Fig. 1. The diffraction pattern of Akdolit-Gran sorbent

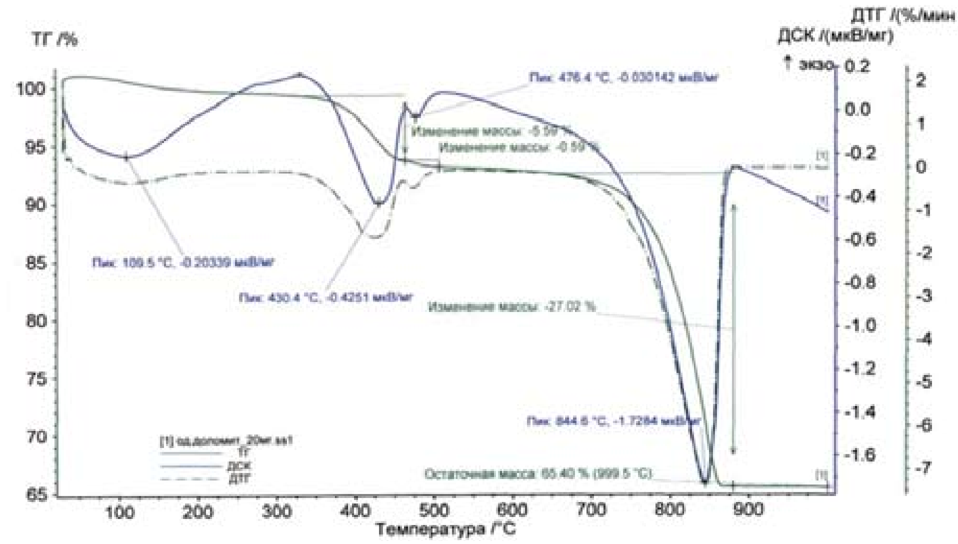

Fig. 2. The thermogram of sorbent Akdolit-Gran: DTC – differential thermogravimetric curve (showing a mass rate of change, this is the first derivative of the TG), TG – thermogravimetric curve, which shows the change-of mass during heating (mass increases or decreases), DSC – differential scanning curve (DSC and DTA show taking place at the on-heating the endo-and exothermic peaks, DTA – analysis from a single point, DSC – analysis with all on-surface)

A thermogram of sorbent sample Akdolit-Gran is shown in Fig. 2. A qualitative identification of the sample was produced according to the number, shape and position of various exo and endo-thermal peaks which are relative to the temperature scale.

Data of the sample thermal analysis show that the DSC curve are observed 4 endoeffect. Slight endoeffect at 109 °C relates to the removal of adsorbed water, endoeffect at 430 °C is caused by dehydration of Mg $(OH)_2$:

$$Mg(OH)_2 \rightarrow MgO+H_2O$$

wherein the sample weight decreases, as the TG curve shows ~ 5.59 % at these temperatures, the compound $Mg(OH)_2$ in a sample of ~ 18 % then is followed by endoeffect at 476 °C, which is caused by dehydration of Ca $(OH)_2$:

$$Ca(OH)_2 \rightarrow CaO+H_2O$$

the weight decreases by 0.59 %, there is a large endoeffect at t = 8440S relating to the decarbonisation of calcite, ie the decomposition of calcite $CaCO_3$ and CO_2 formation:

$$CaCO_3 \rightarrow CaO+CO_2\uparrow$$

the sample weight is reduced approximately 27 %, $CaCO_3$ content of the sample according to the thermogram 61.4 %.

According to the differential thermal and X-ray Akdolit-Gran analysis of sorbent, we can conclude in the process of heat treatment, the chemical transformation also occurs as a result calcium carbonate and magnesium oxide are formed.

The standard techniques of sorbent were determined according to the standard procedures (Table 1). The dose values of proposed sorption material, which were found by experiment, are presented in Table 2.

The experiment (Table 2) showed that the cleaning effect using the sorbent Akdolit – Gran drastically reduced in an acidic medium. The reason of that could be a change of colloid-chemical properties of the sorbent, which the isoelectric point corresponds to approximately pH = 5.4, therefore if the pH values are below this value, the grain of sorbent loses the bimolecular gravitation of binary layer, which causes electrostatic repulsion of metal ions from the sorbent surface by contrast the typical gravitation of the alkaline medium. Furthermore, in the alkaline environment the metal ions are delivered to the reaction centers in the larger mass of sorbent metals.

The amount of copper ions in the sorbent phase (adsorption value) was calculated from A known equation [12].

Table 1. Specifications of the sorbent

Total void content, V_Σ (cm^3/g)	0.103
Bulkdensity, $\rho_н$ (g/cm^3)	1.15
Real density ρ (g/cm^3)	2.37
Average density ρ_0 (g/cm^3)	2.26
Porosity П (%)	4.64
Water absorption W (%)	10.3

Table 2. Results of experiment

№	Reagent dose mg/dm^3	Values pH	Residual concentration Cu^{2+}, mg/dm^3	Residual concentration Ni^{2+}, mg/dm^3	Residual concentration Zn^{2+}, mg/dm^3
1	1.0	3.0	9.736	6.128	4.902
2	1.0	7.0	0.123	1.495	1.295
3	1.0	9.0	1.131	0.183	0.0152
4	1.0	11.0	1.268	0.199	0.0098
5	1.2	3.0	8.131	6.103	3.663
6	1.2	7.0	0.305	0.923	1.306
7	1.2	9.0	0.192	0.163	0.0081
8	1.2	11.0	0.193	0.198	0.0093
9	1.6	3.0	7.961	5.932	3.569
10	1.6	7.0	0.129	0.138	1.0061
11	1.6	9.0	0.109	0.162	0.0062
12	1.6	11.0	0.203	0.204	0.0161
13	2.0	3.0	7.805	5.862	4.998
14	2.0	7.0	0.905	0.132	1.0092
15	2.0	9.0	0.129	0.193	0.0103
16	2.0	11.0	0.151	0.235	0.0198

The absorbtion and concentration of substances from the solution at the surface and in the pores of the sorbent occur at the sorption. A metal distribution coefficient between the solution and carbonate K_d and also the degree of metal recovery from solution were determined. The calculation results are shown in Tables 3, 4.

Sorption ability of Akdolit – Gran differs in relation to the studied materials. The evaluation of the sorbent effectiveness for the metals extraction from aqueous solutions with the help of specific may lead to erroneous conclusions. Thus, evaluation of the effectiveness of heavy metals immobilization with the help of adsorptive capacity values gives the following series of sorption: $Cu^{2+} > Zn^{2+} > Ni^{2+}$, but with the help of a metal distribution coefficient and the degree of metals recovery, we can see the following sequence: $Zn^{2+} > Cu^{2+} > Ni^{2+}$. It is connected with the parameter of adsorptive capacity which depends on mass of the taken sample.

Ionic potential, i.e. the surface charge of the ion can be used to assess the degree of "surface dissociation". The ionic potential is determined by the formula

$$\mathrm{IP} = \frac{n \cdot \mathrm{e}}{r},$$

where n – number of electrons; e – the electron charge.

For Cu^{2+}, Zn^{2+} и Ni^{2+} the number of electrons are 2, and the electron charge is 1.602. There is a relationship the greater ion radius, the lower ionization potential. For Cu^{2+} the atoms radius is 1.278 Å˙, for Zn^{2+} the atoms radius is 1.333 Å˙ and Ni^{2+} the atom radius is 1.246 Å , on that basis, the investigated

Table 3. The sorption capacity of absorption Akdolit – Gran (mg/g)

Number	Dose Akdolit – Gran, g/dm^3	Cu^{2+}	Ni^{2+}	Zn^{2+}
1	1.0	57.74	13.01	19.87
2	1.2	48.16	11.71	16.37
3	1.4	41.28	10.27	14.14
4	1.6	36.76	8.63	12.35
5	1.8	32.26	7.26	10.54
6	2.0	28.15	6.37	9.19

Table 4. The metal distribution coefficient between the solution and sorbent (g/dm3)

Number	Dose Akdolit – Gran, g/dm^3	Cu^{2+}	Ni^{2+}	Zn^{2+}
1	1.0	25.59	6.55	155.23
2	1.2	21.81	12.48	45.98
3	1.4	18.68	16.48	67.98
4	1.6	31.20	7.29	52.55
5	1.8	16.69	3.77	10.28
6	2.0	7.61	2.83	5.64

metals are arranged in series: $Zn^{2+} > Cu^{2+} > Ni^{2+}$, which corresponds to the experimentally obtained data.

Table 5 is shown the kinetic dependence of sorption process of copper ion (II), nickel (II) and zinc (II).

It also gives the following sequence of metals distribution under extraction rate

$$Zn^{2+} > Cu^{2+} > Ni^{2+}$$

It is known that the sorption process is exothermic, as the temperature increases, the sorbent capacity reduces in relation to the metals [14, 15], which is confirmed by the results of Table 6.

The phenomena of the physical and chemical sorption are clearly distinguished in rare cases. Usually, the intermediate options are carried out, when the mass of the adsorbed substance links relatively weakly, and only a small part is firmly [16–18]. The chemical adsorption occurs, as the temperature increases, which begins to overlap the downfall of physical sorption at definite temperature. (Table 7).

These experimental studies were used to develop the project on reconstruction of treatment facilities with the proposed sorption material.

Conclusion

The study's results of sorption properties of natural modified mineral Akdolit – Gran show that it is highly effective sorbent, being relatively cheap natural mineral, which can provide the treatment

Table 5. The degree of metal recovery from solution (%)

Number	Dose Akdolit – Gran, g/dm^3	Cu^{2+}	Ni^{2+}	Zn^{2+}
1	1.0	96.24	86.76	99.36
2	1.2	96.32	93.75	98.22
3	1.4	96.32	95.85	98.96
4	1.6	98.03	92.11	98.92
5	1.8	96.78	87.16	94.87
6	2.0	93.83	84.94	91.86

Table 5. The results of calculation of the rate constant, depending on the reagent dose

Doses mg/dm^3	K, seк$^{-1}$		
	Cu^{2+}	Ni^{2+}	Zn^{2+}
1.0	3.28	2.02	5.05
1.2	3.3	2.77	4.02
1.4	3.3	3.18	4.56
1.6	3.9	2.54	4.44
1.8	3.4	2.05	2.97
2.0	2.78	1.89	2.51

Table 6. The dependence of the adsorptive capacity of the solution temperature, mg/g

Number	Temperature ºC	Cu(II)	Ni(II)	Zn(II)
1	11.5	41.78	10.22	14.06
2	17.0	42.75	10.59	14.28
3	25.0	42.76	10.63	14.26
4	33.0	42.76	10.67	14.28
5	38.5	42.77	10.70	14.27
6	60.0	42.76	10.62	14.22
7	70.5	42.71	10.61	14.20
8	80.0	42.71	10.57	14.14

Table 7. The calculation results of the residual concentration depending on the environmental temperature

Temperature ºC	$C_{ex.}$		
	Cu(II)	Ni(II)	Zn(II)
11.5	2.201	0.689	0.308
17.0	0.151	0.161	0.005
25.0	0.128	0.112	0.031
33.0	0.131	0.056	0.0053
38.5	0.121	0.013	0.0101
60.0	0.136	0.128	0.0805
70.5	0.207	0.146	0.108
80.0	0.210	0.202	0.196

from the complex contamination of heavy metal ions to the required parameters in the purification of circulating water and refuse pulp.

We can draw the following conclusions from the results:

1. It is appropriate to use the sorbent for wastewater electroplating purification by way of a potential sorbention exchanger because the ion exchanger is calcium and magnesium ions.

2. The sorption of cations occurs as the mechanism of ion exchange (the exchange with the cations which are situated in the interstices spaces) and by the formation of complex connections.

3. The optimum dose of sorption material Akdolit – Gran is approximately 1,4–1,6 gr/dm^3 for solutions with initial concentration: Cu (II) = 60 mg/dm^3; Ni(II) = 15 mg/dm^3; Zn (II) = 20 mg/dm^3, temperature conditions are in the range 33,0–38,0 $^{\circ}$C.

4. A treatment effect of using sorbent Akdolit – Gran is drastically reduced in an acidic media.

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