World Applied Sciences Journal 36 (2): 277-286, 2018
ISSN 1818-4952

DOI: 10.5829/idosi.wasj.2018.277.286

Mathematical Model of Industrial Wastewater Cleaning from Heavy Metal Ions Using Acid-Alkali Activated Bentonite

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Abstract: The paper is concerned with industrial wastewater cleaning from heavy metals by natural sorbents. The author developed a method of preparing acid-alkali activated bentonite with high sorption capacity in the form of suspensions and pastes. The experimental method was used to obtain a mathematical model: complete factorial analysis at three levels, the equations that describe the impact of all factors studied are derived.

Key words: Natural sorbents · Heavy metals · Wastewater · Mathematical model

INTRODUCTION

The presence of large deposits of montmorillonite bentonite clays and zeolites allows treating them as the sources of high-quality mineral resources for the production of effective sorbents for the purification of industrial wastewater. This is vital for the Kazakhstan environmental improvement, especially in the mining, ore dressing and metallurgical industrial centers of the Rudny Altai [1].

Natural sorbents have a sorption capacity relative to the polar substances: water, alcohols, amine; as well as a high cation exchange capacity.

Among the unique physical and chemical properties of bentonite in natural conditions of its occurrence are the high dispersion that increases hydrophilicity; the presence of colloid-disperse minerals and sol-gel phases that determine the adhesive properties and plasticity of these species as natural binding materials.

Some natural sorbents are quite active in the natural Condition, but most of them require being activated by chemical or thermal means to increase and regulate their porous structure, changes in the chemical nature of the surface.

One of the largest deposits of bentonite montmorillonite clays is Tagansky deposit in East Kazakhstan.

The bentonites of Tagansky deposit according to the geotechnical classification of M.S. Merabishvili and M.M. Kravchenko were divided into the following lithological horizons:

Horizon 10 - "clay soil", rich in humus, water-soluble iron compounds, silica, organic residues;

Horizon 11- "geochemical barrier" consisting of carbonates of calcium, magnesium, opal, zeolite;

Horizon 12 - "waxy" bleached argillite located directly under the geochemical carbonate-alkaline barrier "breastplate";

Horizon 13 - "spotty" clay, saturated with clusters of mineral ferri-jarosite and psilomelane;

Horizon 14 - "mother" montmorillonite clay and montmorillonite-kaolinite- halloysite. The upper part of the given level (power of 1 to 2.5 m) is rich in soluble organic compounds, so the color becomes black.

Horizon 15 - variegated clays with numerous streaks of quartz-feldspar coarse sand.

One of the most important features of these minerals is the presence of isomorphism, which results in the substitution in the crystal lattice of one cation to another.

Bentonite has a maximum exchange speed (exchange capacity of 80-150 mg / eq per 100 g), which can be explained, firstly, by the maximum dispersion of these minerals and, secondly, by the availability of the exchange of not only external but also internal mineral surfaces.

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In the montmorillonite clays the exchange is being carried out by exchangeable cations of Ca^{++}, Mg^{++}, H^{+}, K^{+}, NH^{3+}, Na^{+} the relative change in the value from $Cà^{++}$ to Na^{+} and exchangeable anions SO_4^{2-}, Cl^{-}, PO_4^{3-}, NO^{3-}.

Studies have shown that such methods of cleaning wastes from heavy metals with the use of bentonite without activation, "Magnafloc 10" composite flocculant and bentonite and thermally activated bentonitane can provide a degree of purification to the level maximum permissible concentration for a fishery (MAC_{fish}).

The author suggests aluminosilicate acid activation technique consisting in acid activation of bentonite by 20% sulfuric acid and neutralization of the aqueous suspension of Horizon 11 bentonite.

The technology for producing aluminosilicate sorbents with increased sorption capacity includes processing bentonite by using acidic reagents under normal conditions. As the acid reactant the 20% sulfuric acid solution with the pH between 1 and 2 was used and as the alkaline reagent - an aqueous suspension of Horizon 11 bentonite.

Being transferred in the result of acid-alkaline activation to the extremely non-equilibrium state, the activated bentonite has a chemically reactive mineral matrix, which, according to the Le Chatelier principle, strives to return to its original stable state. At the same time, there is a process of regeneration (reductive mineralization), which is involved with all kinds of reactive contaminants, that leads to their irreversible chemisorptions binding with silica-alumina sorbent. Colloid-dispersion and the sol-gel phase of hydrolyzed aluminosilicate, that contained in sorbent, provides acceleration of flocculation of the dispersed phase of contaminated liquid and suspended solids in it and colloidal particles followed by their intense. The proposed method allows adding all the required components for cleaning into the water simultaneously. The developed method of cleaning wastewater from heavy metals is focused on the use of cheap natural raw materials in the form of clay rock - aluminosilicates, - which are most environmentally friendly in the environment compared to various chemical reagents.

MATERIALS AND METHODS

To date, pollution of wastewater with heavy metal ions is one of the most serious ecological problems. Heavy metals, many of which are poisonous and carcinogenic, are not decomposed by microorganisms, but rather accumulate in living organisms. In practice, problems associated with the removal of heavy metal ions from water are often solved with the help of reagents that form sparingly soluble compounds with these ions. However, chemical precipitation is not very effective when pollutants are present in trace amounts. To improve the effectiveness of reagent methods of water purification and softening, heterogeneous crystallization on seed particles is sometimes used.

Another method for removing heavy metal ions from water is sorption purification, which can be used for post-cleaning after processing with reagents. As adsorbents, not only activated carbon, silica gels, etc., but also cheap natural sorbents, such as clay, can be used.

In the present work, to increase the efficiency of water purification, it is proposed to combine the processes of heterogeneous crystallization and adsorption using the addition of bentonite, including the one activated by ultrasonic treatment. These processes take place on the interphase surface, which increases and simultaneously is activated by ultrasonic action.

A study of the effectiveness of individual stages and a combined process was carried out in the purification of water contaminated with nickel ions. For the experiments, a solution with an initial concentration of nickel ions of 1 g/l prepared by dissolving 4.95 g/l of $Ni(NO_3)_2 \bullet 6H_20$ in 1 liter of distilled water was used. Working solutions with a concentration of 100 mg/l of 400 ml were prepared by diluting the stock solution. Sodium hydroxide was used as a reagent for precipitation and bentonite clay produced by OOO “Kovcheg SPb” was used as an additive. Preliminary ultrasonic treatment of bentonite particles was carried out in an ultrasonic bath "Sonotech" with a volume of 1 liter and a power of up to 80 W.

First, the sorption properties of bentonite were investigated. A sample of clay was pre-mixed with 40 ml of distilled water to form a slurry. It was then added to the solution with nickel ions and mixed with a magnetic stirrer for 10 minutes. After an hour, the sample was filtered through a paper filter. The concentration of nickel ions was determined by the complex metric method and control checks were made by the atomic-adsorption method.

Quantitatively, the amount of adsorption of solutes on a solid sorbent can be determined by the equation:

$$q_e = \frac{(C_o - C_e)W}{m} \quad (1)$$

where C_i and C_e - initial and equilibrium concentrations of ions in solution, mg/l; m – a mass of sorbent, g; qe - specific adsorption per unit mass of the sorbent, mg/g; V – a volume of solution, l.

The table presents the results of a research of the adsorption of nickel cations on bentonite.

m, g	C_e, mg/l	q_e, mg/l
1.0	85	6.0
2.2	68	5.75
3.9	53	4.84
8.0	26.5	3.68
10.0	14.5	3.42

The sorption properties of the material and the nature of the extraction of certain substances can be judged by sorption isotherms. In particular, the Langmuir isotherm, which assumes a monomolecular layer of adsorbed molecules on the sorbent surface, is described by the equation:

$$q_e = \frac{V_m k C_e}{1 + k C_e} \quad (2)$$

where V_m – monolayer capacity; k - equilibrium constant. The equation can be written in a linear form:

$$\frac{C_e}{q_e} = \frac{1}{k V_m} + \frac{C_e}{V_m}. \quad (3)$$

Experimental data on the absorption of nickel ions (Fig. 1) are described by the dependence (4) corresponding to equation (3):

$$C_e / q_e = 0.133 C_e + 3.09, R^2 = 0.97 \quad (4)$$

In practice, for analysis and calculations, a simple empirical Freundlich equation is often used

$$q_e = K_f C_e^{\frac{1}{m}},$$

where K_f and n - constants. The values of the equation (2) constants found by linear approximation are the following: $K_f = 0.342$, $1/n = 0.11$ with $R_2 = 0.95$.

The small sorption capacity of the investigated bentonite (< 6 mg/g) makes it possible to use it only at the post-purification stage after reagent treatment of sewage with a high content of heavy metals, which in a number of industries exceeds 100 mg/l.

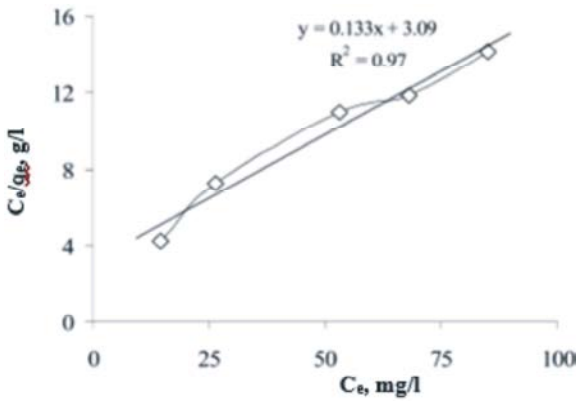

Fig. 1: Isotherm of sorption of nickel ions by bentonite, C_0 = 100 mg/l

Another way is the use of a combined crystallization-adsorption process where the addition of bentonite can perform several functions: primers for heterogeneous crystallization, sorbent and even coagulant

In previous works, it was shown that the optimum concentration of seed additives in heterogeneous crystallization is of the order of 1 g/l.

Therefore, for the combined process, the addition of bentonite at the same concentration was used. Precipitation of nickel hydroxide was carried out with NaOH in a stoichiometric ratio with the content of nickel ions in solution (40 mg). The samples taken during the process were filtered through a paper filter and a membrane filter (in order to avoid small particle breakthrough) and then analyzed. The results of the experiments are shown in Fig. 2.

First, homogeneous crystallization without additives was carried out. The final concentration of nickel ions after purification is 16-17 mg/l. Then, a combined process was carried out with various methods of ultrasonic clay treatment. The duration of ultrasonic treatment is 15 seconds. In one case, the whole solution (400 ml) with nickel ions was subjected to the ultrasonic action, adding a clay suspension and sodium hydroxide as the precipitating reagent. The final cleaning result is 5 mg/l. In the second case, only a suspension of bentonite in 40 ml of a sodium hydroxide solution was subjected to ultrasonic treatment, which was then added to the base solution with nickel ions. At the same time, a much better result was achieved - 0.5 mg/l. In addition, the second option is much more economical.

Preliminary ultrasonic treatment in alkaline solution activates bentonite not only as a result of surface enlargement and renewal but also due to ion exchange

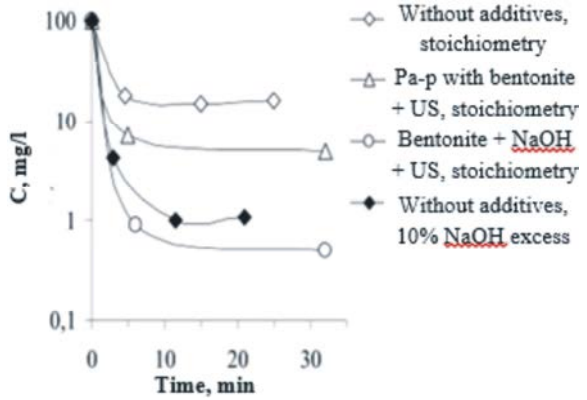

Fig. 2: Kinetics of water purification from nickel ions during crystallization without additives and in a combined process using bentonite and ultrasonic treatment

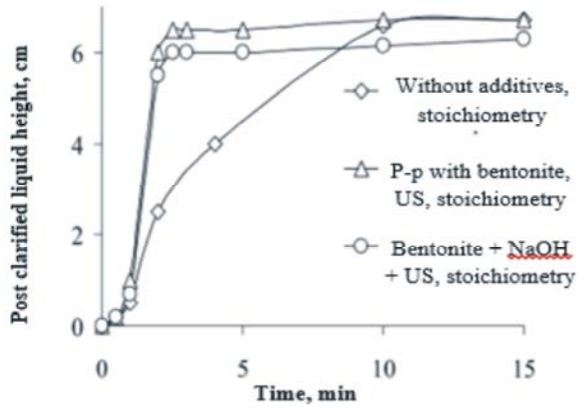

Fig. 3: The rate of precipitation of the solid phase with homogeneous crystallization without additives and in a combined process using bentonite and ultrasonic treatment

processes with the introduction of sodium ions and surface hydroxyl groups into its composition.

For comparison, another experiment with a homogeneous crystallization was conducted, but not with the stoichiometric ratio of alkali and nickel ions, but with a 10% excess of NaOH. Even in this case, the result was worse - the residual content of nickel ions was 1-1.1 mg/l (Figure 2).

The application of ultrasound makes it possible to accelerate not only the crystallization process but also the subsequent sedimentation (Fig. 3). It was observed that short-term irradiation of bentonite promotes coagulation and coarsening of sedimented particles. Intensification of coagulation occurs due to aluminum and iron oxides, which are part of bentonite. Fig. 3 shows a graph of the precipitation of the solid phase in the homogeneous and heterogeneous crystallization of nickel hydroxide. The rate of deposition in the transition to heterogeneous crystallization with the addition of bentonite and ultrasonic action increased from 0.11 to 0.5 mm/s. The thickness of the deposited layer in the case of preliminary ultrasonic treatment of only the alkaline suspension is higher due to the deposition of larger aggregated particles. Thus, the conducted study showed the efficiency of the combined crystallization-adsorption process of water purification from heavy metal ions in which particles of bentonite processed by ultrasound are used as a stimulating additive.

Methods of preparing the acid-alkali activated bentonite that proposed by the author are:

- 20% sulfuric acid in an amount of 100 ml is added to bentonite of Horizons 14 in coma in an amount of 170 g;
- Acid activation takes place within 24 hours;
- Separately, an aqueous suspension of Horizon 11 bentonite is prepared. For this purpose, 170 g of bentonite of Horizon 11 is mixed with 100 ml of distilled water;
- The acid activated bentonite of Horizon 14 is added to an aqueous suspension of Horizon 11 bentonite; this is accompanied by activation of the alkaline sorbent until reaching the pH of 7.5 (water extract).

In the author's research, there was used an activation of sulfuric acid because there is a need in sulfuric acid recycling in the region.

The most effective sorbents for the purification of effluent from the POF of heavy metals are Horizons 14 and bentonite 13, as there is ferri-jarosite mineral in Horizon 14, which is a constituent of $Al_2(SO_4)$ $3iFe_2(SO4)_3$ coagulants.

By the method of activating active adsorbents for the purification, wastewater is produced during activation of bentonite with hot acid for 6 hours.

The sharp increase in activity of acid-treated bentonite, as shown, is connected with the substitution of replacement of cations of sodium, calcium, magnesium with H^+, $A1^{3+}$ and an increase in total acidity exchange and the surface area.

When the acid activated bentonite except for the replacement of exchangeable cations Na^+, Ca^{2+}, Mg^{2+} for hydrogen ions of activating acid, the crystalline structure of montmorillonite is destroyed. In the exchange, position appears H^+ and $A1^{3+}$ ions. Moreover, the exchange of aluminum ions is considerably greater than that of hydrogen ions. The emergence of $A1^{3+}$ is probably due to the extraction of the $A1^{3+}$ from montmorillonite structure

under the action of hydrogen ions of activating acid and binding A13 + with bars to compensate its negative charges. With other conditions being equal, the negative charge of neutralization lattice of montmorillonite $A1^{3+}$ is faster compared to the singly and doubly charged cations.

While in acid treatment of bentonite the value of exchange capacity is reduced, the hydrogen ions activating acid not only displace the exchangeable sodium cations, calcium, magnesium exchange positions, but also penetrate into the interior of the montmorillonite structure and replace magnesium ions, iron, aluminum and other metals from the structure. This is accompanied by the destruction of montmorillonite structure and in the exchange position along with the hydrogen ions appear aluminum cations. Thus a certain amount of silica is released, which leads to a 2-4 fold increase in surface activated samples compared to the surface of natural bentonites. Acid treatment does not change the predominant pore sizes (1.5 nm) of initial bentonite, but gives rise to large pores and transient increase of the sample porosity.

In preparing activated sorbent the aqueous suspension of Horizon 11 bentonite is added, wherein the acid activation of an alkaline sorbent takes place; and as a result there appears mineral of tobermorite - calcium hydro silicate. Calcium silicates formed in the acid-alkali activation are capable of ion exchange. The possibility of isomorphic substitution of Si4 + to Al3 + is typical for bentonite - montmorillonite and calcium silicate.

At acid activation ions of hydrogen and aluminum appear in exchange positions. The montmorillonite structure is destroyed; SiO2 is released, which leads to an increase in available surface for the reacting molecules and the porosity of sorbent. The process of alkali activation is composed of replacement of cations of Ca2+ by hydrogen ions, while exposure to acid removes impurities and achieved by loosening of the structural skeleton.

It is found that in acidic medium the cation exchange flows at a low rate, as a result of adsorption of hydrogen ions of bentonites by themselves. Cationic exchange on bentonites under alkaline conditions is more active than in the neutral ones and in the neutral conditions it is stronger than in the acidic. In the treatment by solution of alkali the amount of hydrogen ions exchanged from the bentonites is larger than by treatment with a solution of a neutral salt. The reason is that in the case of bentonite treatment by an alkali solution the calcium ions are replaced by sodium and hydrogen ions are not only of aluminosilicate complex and hydrogen ions to hydroxides of silicon and aluminum.

Table 1: The factors and ranges of variation

Factors	The value of the factor in the center u_{i0}	The interval of variation δ_i
u_1- contact time, h	1.5	0.5
u_2 - starting concentration, mg/dm3	5.0	2.5
u_3–mass of sorbents, g	25.0	5.0

To create a mathematical model was used an experimental method of obtaining a mathematical model of a full factorial analysis at three levels [2].

Plan an experiment to obtain a regression equation in which the response function of Y1, Y2, Y3 will be the degree of purification of effluents from the heavy metals Pb, Zn, Cu and factors: u1- contact time hours; u2- initial concentration, mg/dm3; u3-mass of sorbent, the resulting equations will determine the individual and combined effect of factors on the degree of purification.

The following factors and ranges of variation were selected for construction of the experimental design (Table 1).

To assess the reproducibility of the plan at each point (each row of the matrix) done by 2 experience, the results of which are designated $y1_j$ and $y2_j$ accordingly. Randomized experiments, but driven by the extended planning matrix are in order. Table 2 shows a matrix of full factorial experiment at three levels (f.f.e. 2^3) in physical variables.

Further processing will be correct in the case of homogeneity of variances. The Cochran's criterion is calculated using the formula (G) (1).

$$G = \frac{S^2_{\max}}{\sum_{j=1}^{8} S_j^2} \quad (1)$$

Because the number of repetitions of the same reproducibility averaged estimate of the variance is defined as the arithmetic average S_{av}, formula (3).

$$S^2_{av} = \sum_{j=1}^{8} f_j S_j^2 / 8 \quad (3)$$

The dispersion of the average value is determined by the formula (4).

$$S^2(\bar{y}) = S^2_{av} / 2 \quad (4)$$

The regression coefficients are found by the formula (5).

$$b_i = \frac{\sum_{j=1}^{8} x_{ij} y_j}{8} \quad (5)$$

The regression equation takes the form of the formula (6).

$$y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{13}x_1x_3 + {}_{12}x_1x_2 + b_{23}x_2x_3 + b_{123}x_1x_2x_3 \quad (6)$$

The interpretation of the equation evaluation of the nature of the influence of factors will be unreliable if insignificant members are not eliminated. That is why the next analysis stage will be testing the hypothesis of the significance of the regression coefficients.

The variance of the regression coefficient is calculated by the formula (7).

$$S^2(b_i) = S^2(\bar{y})/n \quad (7)$$

The boundaries of the confidence interval for the ratio of *b*, within which may deviate from the true value with a given probability δb_i= 0,05 defined by the formula (8).

$$\delta b_i = \pm tS(b_i) \quad (9).$$

Thus, the regression coefficients, smaller in absolute value than δ, can be considered as insignificant.

These members can be excluded from the equation. The orthogonality of the plan is the remaining terms of the equation to the exclusion of insignificant do not change.

Residual dispersion is given by formula (10).

$$S^2_{res} = \sum_{j=1}^{16} (\overline{y_j} - y_j^p)/(n-p) \quad (10)$$

where (n - p) - number of degrees of freedom equal to the number of experiments minus the number of significant coefficients.

The adequacy check is carried out by Fisher's criterion, the formula (11).

$$F_{set} = S^2_{res} / S^2(\bar{y}) \quad (11)$$

If $F_{set} < F_{cr}$ obtained regression equation adequately.

RESULTS AND DISCUSSION

According to Table 1 the experiments were conducted. The results are shown in Tables 2 - 4. Where a column to a final concentration of heavy metal ions, y_{ij} - the degree of purification calculated from the formula (12).

$$y_{ij} = 100\% - \frac{? \cdot 100\%}{C_0} \quad (12)$$

where

C_0-initial concentration, mg / dm^3,

C - residual concentration, mg / dm^3,

i – number of experiments.

Table 2: The degree of purification of the model solution from Zn^{2+} ions, experiment No. 1, 2.

t, h	C_0, mg/dm^3	m,g	C_1, mg/dm^3	C_2, mg/dm^3	y^{zn}_{1j},%	y^{zn}_{2j},%
1	2.5	20	0.81	0.88	67.60	64.80
2	2.5	20	0.40	0.46	84.00	81.60
1	7.5	20	1.85	2.01	75.33	73.20
2	7.5	20	2.83	3.06	62.27	59.20
1	2.5	30	0.84	0.80	66.40	68.00
2	2.5	30	0.80	0.85	68.00	66.00
1	7.5	30	1.78	1.93	76.27	74.27
2	7.5	30	1.13	1.35	84.93	82.00

Table 3: The degree of purification of the model solution from Pb^{2+} ions, experiment No.1, 2.

t,h	C_0, mg/dm^3	m,g	C_1, mg/dm^3	C_2, mg/dm^3	y^{pb}_{1j},%	y^{pb}_{2j},%
1	2.5	20	0.45	0.42	82.10	83.20
2	2.5	20	0.42	0.38	83.20	84.80
1	7.5	20	1.14	0.96	84.80	87.20
2	7.5	20	0.96	1.02	87.20	86.40
1	2.5	30	0.34	0.22	86.40	91.07
2	2.5	30	0.22	0.15	91.07	94.13
1	7.5	30	0.44	0.57	94.13	92.40
2	7.5	30	0.57	0.39	92.40	94.80

Table 4: The degree of purification of the model solution from Cu^{2+} ions, experiments No.1, 2.

t, h	C_0, mg/dm^3	m,g	C_1, mg/dm^3	C_2, mg/dm^3	y_{1j}^{cu},%	y_{2j}^{cu},%
1	2.5	20	0.35	0.40	86.0	84.00
2	2.5	20	0.20	0.23	92.1	90.80
1	7.5	20	0.50	0.36	93.4	95.20
2	7.5	20	0.76	0.54	89.9	92.80
1	2.5	30	0.86	0.93	65.8	62.67
2	2.5	30	0.81	0.85	67.5	65.87
1	7.5	30	1.70	1.93	77.3	74.27
2	7.5	30	1.18	0.98	84.3	86.93

Table 5: Extended matrix of the f.f.e. 2^3

j	y_{1j}^{zn},%	y_{2j}^{zn},%	$\bar{y}_j$,%	$(y_{1j}-\bar{y}_j)^2$	$(y_{2j}-\bar{y}_j)^2$	S_j^2
1	67.60	64.80	66.20	1.,96	1.96	3.92
2	84.00	81.60	82.80	1.44	1.44	2.88
3	75.33	73.20	74.27	1.13	1.13	2.27
4	62.27	59.20	60.74	2.36	2.36	4.71
5	66.40	68.00	6720	0.64	0.64	1.28
6	68.00	66.00	67.00	1.00	1.00	2.00
7	76.27	74.27	75.27	1.00	1.00	2.00
8	84.93	82.00	83.47	2.15	2.15	4.29
					$\sum_{j=1}^{8} S_j^2$	23.35

The Regression Equation for Model Cleaning Solution from the Zinc Ions: Table 5 shows an expanded matrix f.f.e. 2^3, where y_{1j}^{zn},% , y_{2j}^{zn},% degree of purification of cleaning wastewaters from Zn ions, the Table 2.

S_j^2 is according to formula (13).

$$S_j^2 = \frac{\sum_{i=1}^{2}(y_{ij}-\bar{y}_j)^2}{f} \quad (13)$$

Since each S_j^2 dispersion was obtained in two dimensions (y_{1j}^{zn},% , y_{2j}^{zn},%), it corresponds to the number of the degree of freedom f = 1.

Cochran's criterion for the G, the formula (14) is calculated according to the formula (1)

$$G = \frac{4.71}{23.35} = 0.20 \quad (14).$$

The critical value G = 0.6798, (n = 8; f = 1; α = 0.05).

The obtained value of G = 0.20 is less than the critical G = 0.6798, according to this, it's a homogeneous dispersion.

The average estimate of the variance of reproducibility, the formula (15) is calculated according to the formula (3).

$$S_{av}^2 = \frac{23.35}{8} = 2.92 \quad (15).$$

Dispersion of the average meaning, formula (16), is calculated according to the formula (4)

$$S^2(\bar{y}) = 3.07/2 = 1.46 \quad (16).$$

Using Table 3, the regression coefficients are calculated by the average values for the response function (Table 5). Table 6 shows the supporting calculations.

The coefficients of regression equations, formula (17) - (24) are found according to the formula (5)

$$b_0 = 576.95/8 = 72.12 \quad (17)$$

$$b_1 = 11.07/8 = 1.38 \quad (18)$$

$$b_2 = 10.55/8 = 1.32 \quad (19)$$

$$b_3 = 8.93/8 = 1.13 \quad (20)$$

Table 6: Supplementary table

	$x_0\ \overline{y}$	$x_1\ \overline{y}$	$x_2\ \overline{y}$	$x_3\ \overline{y}$	$x_1x_2\ \overline{y}$	$x_1x_3\ \overline{y}$	$x_2x_3\ \overline{y}$	$x_1x_2x_3\ \overline{y}$
1	66.2	-66.2	-66.2	-66.2	66.2	66.2	66.2	-66.2
2	82.8	82.8	-82.8	-82.8	-82.8	-82.8	82.8	82.8
3	74.27	-74.27	74.27	-74.27	-74.27	74.27	-74.27	74.27
4	60.74	60.74	60.74	-60.74	60.74	-60.74	-60.74	-60.74
5	67.2	-67.2	-67.2	67.2	67.2	-67.2	-67.2	67.2
6	67	67	-67	67	-67	67	-67	-67
7	75.27	-75.27	75.27	75.27	-75.27	-75.27	75.27	-75.27
8	83.47	83.47	83.47	83.47	83.47	83.47	83.47	83.47
Ó	576.95	11.07	10.55	8.93	-21.73	4.93	38.53	38.53

Table 7: Values Y_j^{Zn} and $\overline{y_j} - Y_j^{Zn}$ according to the regression equation

$\overline{y}_j$,%	Y_j^{Zn}	$(\overline{y_j} - Y_j^{Zn})^2$
66.20	65.65	0.30
82.80	83.39	0.35
74.27	73.69	0.34
60.74	61.35	0.37
67.20	67.89	0.48
67.00	66.27	0.53
75.27	75.89	0.38
83.47	82.91	0.31
Σ		3.07

$$b_{12}=-21.73/8=-2.72 \quad (21)$$

$$b_{13}=4.93/8=0.62 \quad (22)$$

$$b_{23}=38.53/8=4.82 \quad (23)$$

$$b_{123}=38.53/8=4.82 \quad (24)$$

The regression equation takes the form of the formula (25).

$$y = 72.12 + 1.358x_1 + 1.32x_2 + 1.13x_3 - 2.72x_1x_2 + 0.62x_1x_3 + 4.82x_2x_3 + 4.82x_1x_2x_3$$

Interpretation of the equation: the assessment of the nature of the influence of factors will be unreliable if insignificant members are not eliminated.

The variance of the regression coefficient, the formula (26) is found according to the formula (7).

$$S^2(b_i) = 1.46/8 = 0.18 \quad (26)$$

And then the dispersion takes the following form, the formula (27)

$$S(b_i) = \sqrt{0.18} = 0.42 \quad (27)$$

Student's coefficient for n = 8, α = 0.05 t = 2.31. According to the formula (9) the boundaries of the confidence interval are determined for the bi ratio within which bi, may deviate from the true value with a given probability α = 0,05 is, the formula (28):

$$\delta b_i = \pm t \cdot S(b_i) = \pm 0.42 \cdot 2.31 = \pm 0.97 \quad (28).$$

Thus, the regression coefficients, which are smaller in absolute value than 0.97 can be considered significant. In the resulting equation the insignificant members will be: b_{13} = 0.62. These members are excluded from the equation, the formula (29):

$$Y^{Zn} = 72.12 + 1.38x_1 + 1.32x_2 + 1.13x_3 - 2.72x_1x_2 + 4.82x_2x_3 + 4.82x_1x_2x_3 \quad (29)$$

Checking the adequacy of this equation. For each matrix row Y_j^{Zn} is found and the residuals $\overline{y_j} - Y_j^{Zn}$ are calculated. The results are summarized in Table 7.

The residual variance, the formula (30) is defined according to the formula (10).

$$S_{set}^2 = 3.07(8-7) = 3.07 \quad (30),$$

where (8 - 7) is the number of degrees of freedom equal to the number of experiments minus the number of significant coefficients. Fischer's calculated value, formula (31), is found according to the formula (11).

$$F_{res} = 3.07/1.46 = 2.10 \quad (31).$$

Tabulated value of the Fisher's criterion for significance level of 0.05; $f_1 = 1$; $f_2 = 8$ is equal to 5.32, as F calculated $<F_{cr}$; 2.10<5.32, the obtained regression equation is adequate.

The transition from the encoded xi to the natural values of the variables ui is made according to the formula:

$$x_i = \frac{u_i - u_{i0}}{\delta_i} \quad (32)$$

The transition from coded variables to the natural ones is made according to the formula (32). The regression equation takes the form, the formula (33).

$$Y^{Zn} = -196.57 + 206.15u_1 + 51.82u_2 + 4.05u_3 - 40.7u_1u_2 - 3.85u_1u_3 - 0.76u_2u_3 + 0.77u_1u_2u_3 \quad (33)$$

Results of the Tables 3-4 were treated analogously. And, the following regression equation:

Degree model solution purification from ions Pb^{2+}

$$Y^{Pb} = 62.92 + 1.44u_1 + 0.51u_2 + 0.85u_3 \quad (34)$$

Degree model solution purification from Cu^{2+} ions.

$$Y^{Cu} = 89.93 + 35.4u_1 + 9.33u_2 - 0.93u_3 - 8.5u_1u_2 - 1.26u_1u_3 - 0.29u_2u_3 + 0.34u_1u_2u_3 \quad (35)$$

Field experiment tests were conducted in the laboratory of Berezovskaya polymetallic processing plant which is located in the East Kazakhstan region. The mine water which was used to feed the recycled water processing factory was used as the effluent.

Using the regression model of solution purification, achieved with the help of a full factorial design on three levels, we find the required amount of sorbent for purification of effluents from the lead, copper and zinc ions.

According to the formula (36) we define the necessary degree of purifying the wastes from α1 lead, α2 zinc, a3 copper ions, which correspond to the MAC_{fish}. Formula (37) - (39).

$$Y_{set} = \frac{C_0 - MAC_{fish}}{C_0} \quad (36)$$

where C_0 is the initial concentration of heavy metal in the model solution;

MAC_{fish} - allowable concentrations for fishery use.

$$Y_{set}^{Pb} = \frac{2.1 - 0.1}{2.1} \cdot 100\% = 95.23\% \quad (37)$$

$$Y_{set}^{Zn} = \frac{4.7 - 0.01}{4.7} \cdot 100\% = 99.78\% \quad (38)$$

$$Y_{set}^{Cu} = \frac{3.5 - 0.001}{3.5} \cdot 100\% = 99.97\% \quad (39)$$

From the formula (34) the required amount of sorbent is defined, $Y^{Pb}{}_{set}$ is the degree of purification of effluents from lead ions, u_1 - contact time of sorbent, 2 hours, u_2 is the initial concentration of 2.1 mg / dm^3, the formula (40).

$$u^{Pb}{}_3 = \frac{Y_{set}^{Pb} - 61.92 - 1.44u_1 - 0.5u_2}{0.85} = 34 \quad (40)$$

From the formula (33) the required amount of sorbent is defined, $Y^{Zn}{}_{set}$ is the degree of purification of effluents from the Zinc ions, u_1 - contact time of sorbent, 2 hours, u_2 - the initial concentration, 4.7 mg / dm^3, the formula (41).

$$u^{Zn}{}_3 = \frac{Y_{set}^{Zn} + 196.57 - 206.15u_1 - 51.82u_2 40.7u_1u_2}{(4.05 - 3.85u_1 - 0.76u_2 + 0.77u_1u_2)} = 36 \quad (41)$$

From the formula (35) the required amount of sorbent is defined, $Y^{Cu}{}_{set}$ is the degree of purification of effluents from the copper ions, u_1- contact time of sorbent, 2 hours, u_2 - the initial concentration 3.5 mg / dm^3, the formula (42).

Table 8: Activation of the bentonite by 20% sulfuric acid and by neutralization of aqueous bentonite slurry of Horizon 11, the experiment series No.1

	Concentration of Cu^{2+},mg/dm^3			Concentration of Pb^{2+},mg/dm^3			Concentration of Zn^{2+},mg/dm^3		
Sorbent	$C_{original}$	$C_{residual}$	Degree of purification α,%	$C_{original}$	$C_{residual}$	Degree of purification α,%	$C_{original}$	$C_{residual}$	Degree of purification α,%
Horizon 14	3.5	0.001	99.97	2.1	0.1	95.24	1.9	0.01	99.47
Horizon 13	3.5	0.001	99.97	2.1	0.1	95.24	1.9	0.01	99.47

Table 9: Activation of the bentonite by 20% sulfuric acid and by neutralization aqueous bentonite slurry of Horizon 11, the experiment series No.2

	Concentration of Cu^{2+},mg/dm^3			Concentration of Pb^{2+},mg/dm^3			Concentration of Zn^{2+},mg/dm^3		
Sorbent	$C_{original}$	$C_{residual}$	Degree of purification α,%	$C_{original}$	$C_{residual}$	Degree of purification α,%	$C_{original}$	$C_{residual}$	Degree of purification α,%
Horizon 14	3.5	0.001	99.97	2.1	0.12	94.29	1.9	0.01	99.47
Horizon 13	3.5	0.001	99.97	2.1	0.13	99.81	1.9	0.01	99.47

Table 10: Activation of the bentonite by 20% sulfuric acid and by neutralization by aqueous bentonite slurry of Horizon 11, the experiment series No.3

	Concentration of Cu^{2+},mg/dm^3			Concentration of Pb^{2+},mg/dm^3			Concentration of Zn^{2+},mg/dm^3		
Sorbent	$C_{original}$	$C_{residual}$	Degree of purification α,%	$C_{original}$	$C_{residual}$	Degree of purification α,%	$C_{original}$	$C_{residual}$	Degree of purification α,%
Horizon 14	3.5	0.001	99.97	2.1	0.15	92.86	1.9	0.01	99.47
Horizon 13	3.5	0.001	99.97	2.1	0.11	94.76	1.9	0.01	99.47

$$u^{Cu}{}_3 = \frac{Y_{set}^{Cu} - 89.93 - 35.4u_1 - 9.33u_2 + 8.5u_1u_2}{(-0.93 - 1.26u_1 - 0.29u_2 + 0.3u_1u_2)} = 14.34 \quad (42)$$

According to the regression equation (40-42), to reach the MAC for heavy metals (Cu^{2+}, Pb^{2+}, Zn^{2+}) the maximum weight of sorbent must be 36 gram. Also, a series of experiments on the purification of the effluent from heavy metals where the mass of sorbent is 36 gram were conducted. The results are shown in Tables 11-13.

CONCLUSION

The uses of acid-alkaline which were activated by the bentonite in the purification of industrial wastewater from heavy metals will improve cleaning efficiency and the resulting equations will allow to calculate the required amount of sorbent and thereby to reduce the consumption of sorbents.

The technology of production of silica-alumina, bentonite sorbents in the form of a sorption-active paste of bentonite subjected to acid-alkaline activation was developed.

A mathematical model of sorption purification of effluent from the heavy metal ions (Cu^{2+}, Pb^{2+}, Zn^{2+}) was built.

The degree of purification depends on the initial concentration of the solution, the mass of sorbent and time of contact of sorbent with the solution.

The regression equations describing the process of cleaning wastes in the effluents from heavy metals in the f (Cu^{2+}, Pb^{2+}, Zn^{2+}) were derived.

Pilot-scale studies on the cleaning in the Berezovskaya Polymetallic concentrator.

The results showed that the degree of purification from Pb^{2+} ions – 92.86%, $Zn^{2???+}$ - 99.47% and Cu^{2+} 99.97%.

REFERENCES

1. Abronisimov, D.O. and S.I. Lazarev, 2014. Application of Membrane Technology in Wastewater Treatment of Electroplating Industry – Bulletin of Tambov State Technical University, 2(20): 306-312.
2. Bayburdov, T.A., I. Berizovskaya Ye, *et al*., 2015. Using Polymeric Sorbent Technologies for Ecology Monitoring of Water Objects – News of Saratov University, 1(15): 36-42.