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Sergii Guzii*
State Institution "Institute of Environmental Geochemistry" of the National Academy of Sciences of Ukraine
https://orcid.org/0009-0009-4635-2806

Andriy Tovmachenko
State Institution "Institute of Environmental Geochemistry" of the National Academy of Sciences of Ukraine
https://orcid.org/0000-0002-0674-8410

Volodymyr Viter
State Institution "Institute of Environmental Geochemistry" of the National Academy of Sciences of Ukraine
https://orcid.org/0009-0005-2551-9495

Modelling of Organo-Mineral Complexes in the System "Lime-Zeolite-Enzyme" for Purifying Technically Polluted Water from Suspended Solids and Compacting Sediment

Abstract. The article presents the results of experimental and statistical modelling to determine the optimal composition of organo-mineral complexes for cleaning technically polluted water from suspended solids and compacting sediment in storage ponds at solid waste landfills during their reclamation and reconstruction. Water transparency with a turbidity index of 1.55 NTU they ensured by using an organo-mineral complex containing 7.25-8.25% quicklime, 2.5-3% zeolite and 7.5-8.25% enzyme. Sedimentation in the form of a sediment with a tensile strength of up to 160 kPa on the 28th day of exposure they ensured by using an organo-mineral complex containing 30.63-35% quicklime, 0-3.5% zeolite and 0-1.25% enzyme.

Keywords: technically contaminated water, suspended solids, turbidity/transparency, sediment, plastic strength, mathematical models, optimisation, organo-mineral complex, enzyme, zeolite.

*Corresponding author E-mail: sguziy2@gmail.com

Introduction.

In modern conditions, measures to treat the suspension of technically polluted water, especially from solid waste storage landfill ponds, are very relevant. These measures will help to produce clean water for small and large cities. Such waters are usually muddy and contain suspensions of viscous liquids from petroleum products, oils, clay particles, microscopic algae (phytoplankton), bacteria and dissolved organic and colloidal solids that colour water [1]. The suspension, treated with coagulants and forming a sediment with certain physical and mechanical properties, can be use to reconstruct storage ponds and subsequently expand and reclaim them.

Literary review and problem statement.

Works [2, 3] show that in the primary water flows of drainage systems, the average deposition of fine sediments increases almost six fold upstream, and the maximum turbidity values for single drainage operations exceed 460 nephelometric turbidity units (NTU). The use of physical mitigation structures prevents suspended solids from entering the receiving stream, significantly reducing the inflow and rate of sedimentation.

The effectiveness of using natural coagulants to eliminate turbidity in pond water has been note at a level of 78.58-94.18% with a long settling time [4].

In [5], a modified horizontal clarifier with rotating biological discs for treating slightly polluted surface water was proposed and developed. Its effectiveness in simultaneously removing turbidity, organic matter and NH^{+4}-N we noted. The results show that the quality of wastewater from the modified clarifier remains stable for more than two months of continuous operation. With a hydraulic retention time (HRT) of 2.0 hours, the modified clarifier was able to remove $73.65 \pm 5.15\%$ of turbidity, $53.98 \pm 5.17\%$ total organic carbon (TOC) and $77.01 \pm 10.02\%$ NH^{+4}-N with an average turbidity level of 1.96 NTU, 1.98 mg/L TOC and 0.46 mg/L NH^{+4}-N residue in the wastewater.

Study [6] evaluated the effectiveness of polyacrylamide (PAM) injection in reducing wastewater turbidity. The results showed that cationic PAM was the most effective in reducing turbidity, followed by non-ionic PAM. Cationic and non-ionic PAMs injected into the pumped turbid water reduced the turbidity of the wastewater from the basin by 98% and 90%, respectively.

According to the results of in situ testing [7] of the coagulation-sedimentation-filtration process, satisfactory water purification efficiency we established in terms of turbidity and TP. The optimal dosages of polyaluminium chloride (PAC) and PAM were determined to be 50 ppm and 1.5 ppm, respectively. The treatment process achieved an exceptional removal efficiency of 99.53% for turbidity and 94.69% for total phosphorus (TP), resulting in wastewater with a stabilised turbidity of < 1 NTU and a TP concentration of up to 0.017 mg/L, which fully complies with Class II for EQSSW.

In [8], the applicability of electrocoagulation technology using iron-aluminium (Fe-Al) electrodes for the effective treatment of wastewater from aquaculture ponds we verified. The study of the influence of various parameters on the electrocoagulation process, such as initial pH, charging time and settling time, on the removal of turbidity from aquaculture wastewater (AW) at an initial pH of 8 and a temperature of 30°C was optimised using the response surface methodology (RSM) with the Box-Benken design (BBD). The optimal conditions were a charging time of 11.970 min, a settling time of 29.994 min, and a current density of 2.389 A, which resulted in 91.84% turbidity removal at 30°C for 500 ml of wastewater. The correlation between the predicted value (91.84%) and the measured value (91.67%) confirms the reliability of the results predicted by the quadratic regression model.

According to research [9], it was found that coagulation alone is not sufficient for natural stone (travertine) processing wastewaters (NSPW) treatment, while flocculation and coagulation with flocculation provided excellent treatment. Among the coagulants used, $AlCl_3$ showed the best result in terms of turbidity removal by coagulation with NSPW at pH 6 and 9, while the turbidity removal efficiency of the three coagulants was almost identical at pH 7.5. In addition, a relatively low pH (i.e. pH 6) improved the purification efficiency of all coagulants. During NSPW coagulation at pH 6, the charge neutralisation mechanism played a decisive role in turbidity removal. However, in neutral (pH 7.5) and slightly alkaline (pH 9) environments, the coagulation mechanism with removal prevailed. For NSPW flocculation, the main mechanism was the formation of polymer bridges.

The authors [10] optimised the performance of sedimentation tanks by studying geometric parameters, flow rate and sediment characteristics. The resulting mathematical models predict the behaviour of the system under different conditions, contributing to stable operation through optimised temperature, reagent dosing and sediment management. The experimental approach determines the optimal reagent and temperature settings for water purification, ensuring stable results. Key performance indicators – water turbidity, suspended solids concentration and sedimentation rate – they related to operational variables.

In [11], the processes of purifying the liquid phase of a sedimentation tank at a solid waste landfill in Mariupol we studied. To purify wastewater from iron ions, it we proposed to use a precipitation method by increasing the pH, which leads to the binding of hydroxides by sediment. Calcium hydroxide and metallurgical slag are use as a neutralising mixture. To remove phenols, sorbents - layered double hydroxides - they proposed. The processes of sediment formation - an asphalt-like layer - they studied. The parameters for the safe conduct of the neutralisation process they studied, preventing pollutants from entering the air.

In [12], it we noted that atmospheric precipitation is the main source of filtrate formation, and storm water management is crucial to minimising its formation. The authors propose a system for removing filtrate from storm water, which includes a drainage layer constructed above the lower anti-filtration screen. The drainage layer ensures the accumulation and movement of filtrate. As a rule, a network of pipes they installed in the drainage layer to transport the filtrate to the collection point. The bottom of the landfill should have a slope to ensure the movement of filtrate to the drainage pipes.

Paper [13] presents the results of laboratory tests on the compaction and shear strength of silty soils with the addition of 0–8% lime and/or cement by mass of dry soil. Studies we conducted on samples with an optimal moisture content, after 7 and 14 days of air-water treatment including freeze-thaw cycles. The introduction of hydraulic binders we found to significantly alter the compaction parameters and increase the shear strength, particularly the angle of internal friction and cohesion. The effectiveness of stabilisation depended largely on the type of binder used, the soil's granulometric composition and the treatment regime applied to the samples.

The above data reveals the objective of this work: to carry out experimental and statistical modelling of the organo-mineral complex for sedimentation in technically polluted waters. The goal is to be achieve by solving the problems of water purification from turbidity and obtaining sediments with specified plastic strength indicators, which will allow them to be use for building pond banks, as well as for compacting water-saturated loose sands and non-plastic silty soil deposits.

Materials and methods. Water Sampling. The studies we conducted using water contaminated by Storage Pond No. 1 (Fig. 1) on the land plot of the Solid Waste Landfill (SWL) in Chernihiv, Ukraine.

The sanitary and hygienic assessment of water quality is presented in Table 1 and Table 2 (based on the data of Measurement Protocols Nos. 1528 and 1528/P dated 15.07.2025, LLC "EKODIYA", Kyiv).

Figure 1 - Area of interests.

As can be seen from the data in Tables 1 and 2, technically contaminated water is characterised by a complex anion-cation composition and is a dispersed system in which oil-like substances they evenly distributed in salt-saturated water. The presence of a suspension of high-molecular compounds causes its turbidity.

Selection of Precipitating Reagents.

For precipitation, quicklime we used as an active mineral substance, which, interacting with anions, will promote the formation of water-insoluble precipitates. Zeolite we used as an adsorbent, which will promote the sorption of oils, surfactants and radiation sources. Enzyme (ECO-NOVA GmbH, Germany) was used as a highly effective industrial enzyme preparation for transesterification and cleavage of fats, petroleum products, etc., which also promotes the binding of aluminosilicate octahedrons of zeolite into water-insoluble layers with a water-repellent effect [14, 15].

Experimental and Statistical Modelling.

The optimisation of the organo-mineral complex compositions for the precipitation of technically contaminated water was carried out using three-factor simplex central planning of experiments in the STATISTICA 12 mathematical environment with the implementation of a special cubic model that considers the non-linearity of the influence of factors on the properties of the initial parameters.

The coefficients of variation and the matrix for planning the experiment they given in Tables 3 and 4, and the implementation of the experiment we given in Tables 5 and 6.

Table 1 - Chemical composition of water

Indicator name	Units of measurement	Results	Measurement uncertainty estimation
Hydrogen index	pH Units	8.32	±0.05pH
Suspended solids	mg/L	63	±10%
Dry residue	mg/L	6708	±10%
Phosphates (PO_4^{3-})	mg/L	5.95	±10%
Sulphates (SO_4^{2-})	mg/L	670	±10%
Sulphides (S_2^-)	mg/L	<0.01	±22%
Chlorides (Cl^-)	mg/L	2510	±15%
Ammonium (NH_4^+)	mg/L	111	±9%
Nitrites (NO_2^-)	mg/L	0.05	±25%
Nitrates (NO_3^-)	mg/L	1.60	±25%
Total Fe	mg/L	2.95	±10%
COD	mgO/L	643	±15%
BOD	mgO/L	308	±25%
Anionic Surfactans	mg/L	1.34	±25%
Oil products	mg/L	0.42	±25%
Fats and oils	mg/L	4.0	±32%
Mn	mg/L	0.07	±23%
Cu	mg/L	1.38	±15%
Ni	mg/L	1.25	±18%
Zn	mg/L	0.03	±22%
Cd	mg/L	<0.01	±25%
Pb	mg/L	<0.01	±21%
Ag	mg/L	1.65	±20%
Al	mg/L	2.95	±20%
Total Cr	mg/L	2.35	±23%
Cr 6 (CrO_3)	mg/L	0.08	±35%

Table 2 - The radiation assessment of water quality

Indicator name	Units of measurement	Results	Measurement uncertainty estimation, δ
$\sum \alpha$-activity	Bq/L	0.38	±0.05
$\sum \beta$-activity	Bq/L	1.24	±0.10
Specific activity Rn-222	Bq/L	<0.3	-

Table 3 - Variation intervals and values of variable factors

Factors, type	Natural	Coded	Levels of variation		Variation interval
			0	1	
CaO	%	X1	0	35	17.5
Zeolite	%	X2	0	15	7.5
Enzyme	%	X3	0	10	5

Table 4 - Experiment planning matrix

Plan points	Matrix plan in codes			Full size matrix plan		
	X1	*X2*	*X3*	CaO	Z	E
1	0.00	1.00	0.00	0	15	0
2	0.33	0.33	0.33	11.7	5	3.3
3	1.00	0.00	0.00	35	0	0
4	0.50	0.50	0.00	17.5	7.5	0
5	0.00	0.00	1.00	0	0	10
6	0.50	0.00	0.50	17.5	0	5
7	0.00	0.00	0.50	0	7.5	5

Table 5 - Correspondence of coded values to natural values

Coded	Natural		
	CaO (*X1*)	Zeolite (*X2*)	Enzyme (*X3*)
0	0	0	0
0.25	8.75	3.75	2.5
0.5	17.5	7.5	5
0.75	26.25	11.25	7.5
1.0	35	15	10

Table 6 - Results of the implementation of the experimental plan

Plan points	Turbidity, NTU, after day			Tensile strength, kPa, after day		
	14	21	28	14	21	28
1	185	172	92	0.1	1.81	3.42
2	647	629	127	0.2	0.8	1.06
3	1000	1000	1000	1.49	40.4	158.3
4	1000	1000	1000	0.96	29,82	89.8
5	183	17.1	1.55	0	0	0
6	586	533	315	0.1	0.87	1.41
7	213	211	175	0,1	0.48	0.62

Results. Determination of Water Turbidity. Because of mathematical processing of the experimental results (Table 6), experimental statistical models we obtained in the form of regression equations (1-3), which reflect the influence of the varied factors of the organo-mineral complex on the change in water turbidity on the 14th, 21st and 28th days of exposure:

$$T^{14d}=1000X1+185X2+183X3+1630X1X2-22X1X3+116X2X3-15X1X2X3 \quad (1)$$

$$T^{21d}=1000X1+172X2+17.1X3+1656X1X2+97.8X1X3+465.8X2X3-377,7X1X2X3 \quad (2)$$

$$T^{28d}=1000X1+92X2+1.55X3+1816X1X2-743.1X1X3+512.9X2X3-11170.35X1X2X3 \quad (3)$$

Based on regression equations, terminal surfaces of water turbidity change depending on the influence of varied factors of the organo-mineral complex (Figs. 2–4) with conditional designations of indicators (Table 4) were constructed. It should be noted that the components of point's 3 and 4 (Table 6) completely absorbed water, so their turbidity values were taken as 1000 NTU.

Analysis of regression equations (1–3) and Pareto effect diagrams showed that turbidity indicators after 14, 21 and 28 days of ageing are influenced by three main factors of variation $X1$, $X2$ and $X3$, which account for up to 80% of the total impact (see Fig. 2b, 3b and 4b). While the products of factors $X1X2$, $X2X3$ and $X1X2X3$ contribute 20% of the total influence of factors on the turbidity index. According to the expected reactions (Figs. 2c, 3c and 4c), factors $X2$ and $X3$ have the most significant impact on the reduction of the turbidity index. On days 21 and 28 of the test, the influence of factor X3 approaches 0, which is associated with the end of the enzyme's action in the decomposition of petroleum bitumen, fats, oils and organic suspensions in water.

In Fig. 2a shows that the decrease in water turbidity from 647 to 183 NTU on the 14th day of exposure is influenced by a decrease in the content of quicklime ($X1$) from 17.5% to 0%, an increase in the zeolite content ($X2$) from 12% to 15%, and an increase in the enzyme content ($X3$) from 0% to 10%.
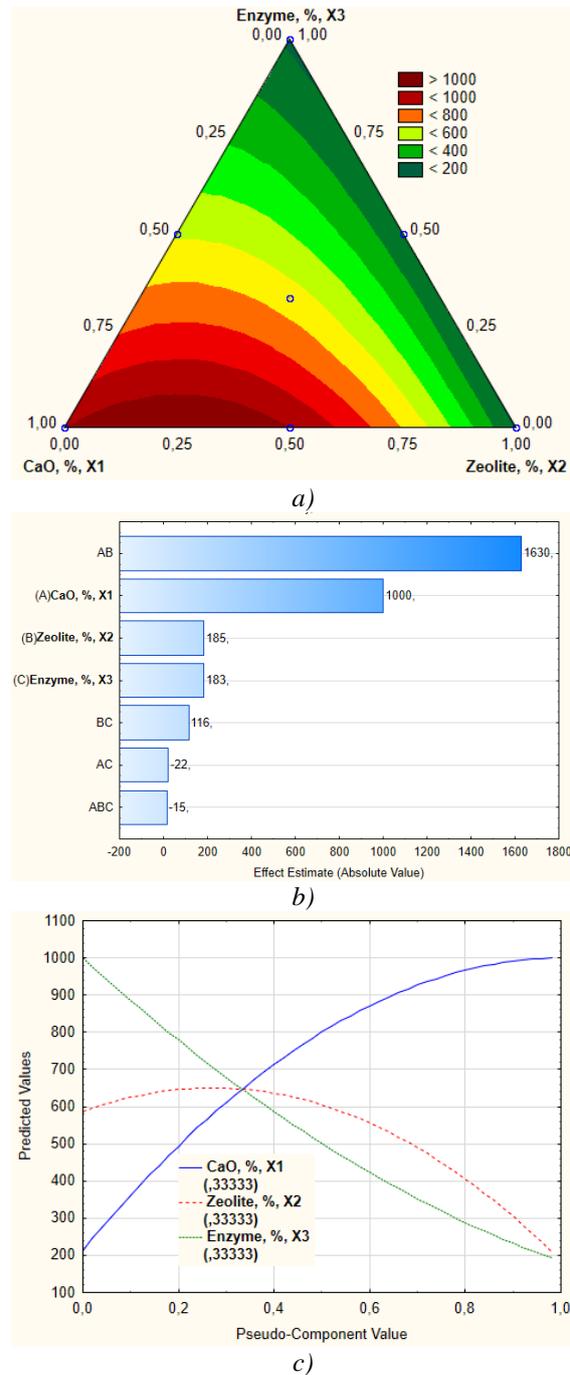

a)

b)

c)

Figure 2 - Ternary surfaces (a), Pareto diagram (b) and expected reactions (c) of water turbidity on the 14th day of exposure to factors of the organo-mineral complex

To reduce water turbidity from 533 to 17.1 NTU on the 21st day of exposure (Fig. 3a) is influenced by the content of the organo-mineral complex components, namely: the amount of quicklime 0–13.3% ($X1$), the amount of zeolite 13.5–15% ($X2$) and the amount of enzyme 0–10% ($X3$).
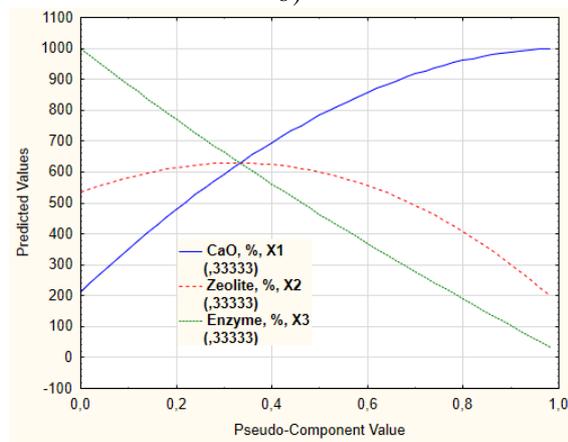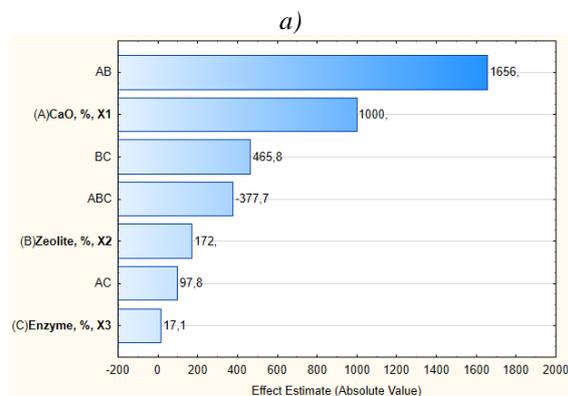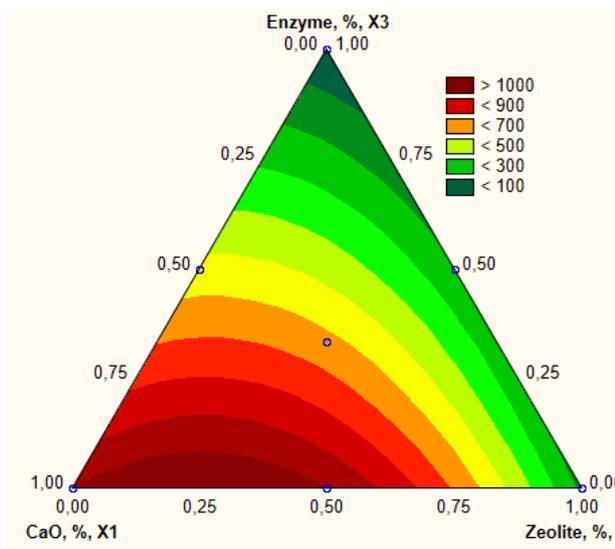
a)

b)

c)

Figure 3 - Ternary surface (a), Pareto diagram (b) and expected reactions (c) water turbidity on the 21th day of exposure to factors of the organo-mineral complex

To reduce water turbidity from 313 to 1.55 NTU on the 28th day of exposure (Fig. 4a), after which the water becomes transparent, the contents of the organo-mineral complex are added, namely: quicklime from 0 to 15% (*X1*), zeolite from 0 to 8.75% (*X2*) and enzyme from 4.17 to 10% (*X3*).
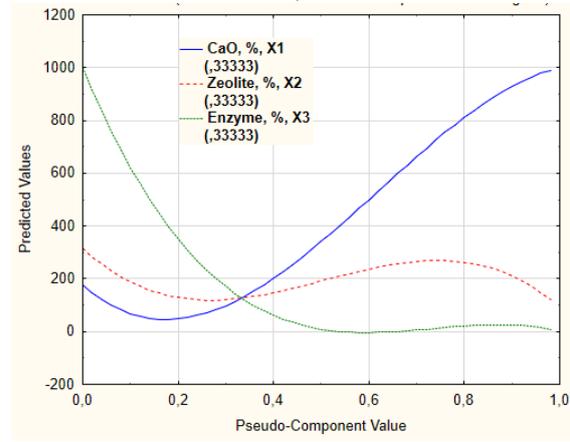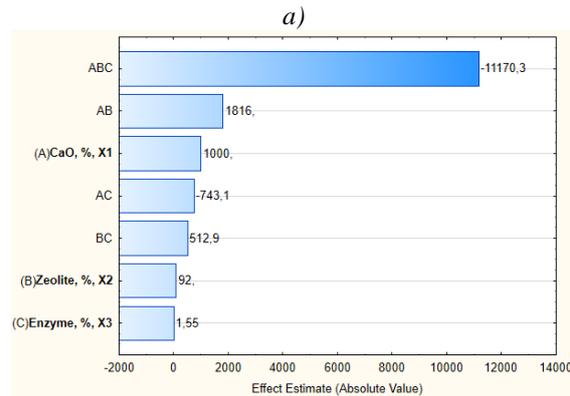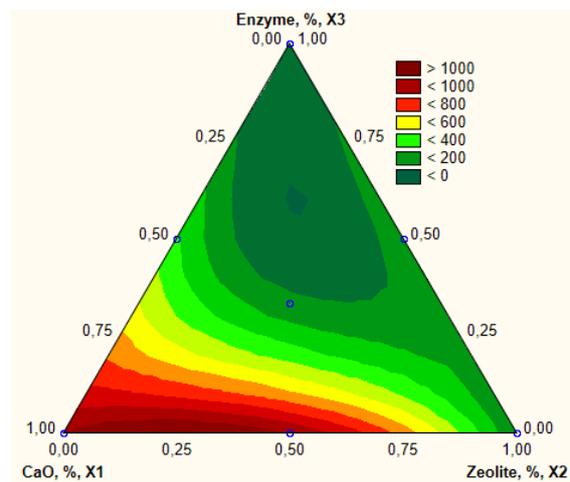

a)

b)

c)

Figure 4 - Ternary surface (a), Pareto diagram (b) and expected reactions (c) water turbidity on the 28th day of exposure to factors of the organo-mineral complex

By superimposing terminal surfaces on each other (taking into account the criterion value of turbidity (T→0)), the optimal range of the component composition of the organo-mineral complex was determined. The region is limited along the *X1* axis by the amount of quicklime from 7.25 to 8.25%, along the *X2* axis by the amount of zeolite from 2.5 to 3%, and along the *X3* axis by the amount of enzyme from 7.5 to 8.25% (Fig. 5).

The composition of the organo-mineral complex in a given area ensures the production of transparent water with a turbidity level of no more than 1.55 NTU.
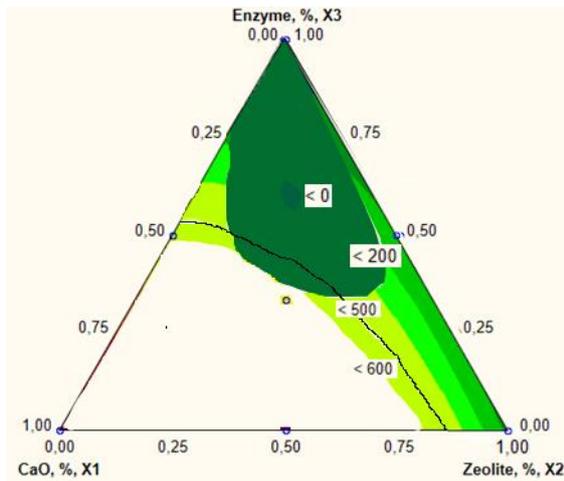
Figure 5 – Combined diagram showing the influence of factors affecting the organo-mineral complex on changes in the turbidity index of technically polluted water

Determination of the Tensile strength of Sediment.

As a result of mathematical processing of the experimental results (Table 6), experimental and statistical models were obtained in the form of regression equations (4-6), which reflect the influence of the varied factors of the organo-mineral complex on the change in the tensile strength of the sediment on the 14th, 21st and 28th days of exposure:

$$Ts^{14d}=1.49X1+0.1X2+2.9E\text{-}16X3+0.66X1X2-2.58X1X3+0.2X2X3-3.75X1X2X3 \quad (4)$$

$$Ts^{21d}=40.4X1+1.81X2+5.2E\text{-}15X3+34.86X1X2-77.32X1X3-1.7X2X3-225.81X1X2X3 \quad (5)$$

$$Ts^{28d}=158.3X1+3.42X2-2.4E\text{-}14X3+35.76X1X2-310.96X1X3-4.36X2X3-588.18X1X2X3 \quad (6)$$

Based on regression equations, terminal surfaces of changes in the plastic strength of the precipitated suspension we constructed depending on the influence of varied factors of the organo-mineral complex as seen in Figures 6 – 8 with conditional designations of factor indicators (Table 4). When determining the tensile strength, point 5 (Table 6) did not form sediment, so its value was taken as 0.

Analysis of regression equations (4–6) and Pareto effect diagrams showed that the tensile strength of sediment after 14, 21 and 28 days of exposure is influenced by two main factors of variation, *X1*, *X2* and the product of factors *X1X2*, which account for up to 80% of the total impact (see Figures 6b, 7b and 8b). Factor *X3* and the products of factors *X2X3* and *X1X2X3* contribute 20% of the total influence of factors on the tensile strength of the sediment. According to the expected reactions (Figs. 6c, 7c and 8c), factor *X1* has the most significant effect on increasing the tensile strength of the sediment. The effect of factors *X2* and *X3* is insignificant.

As shown in Fig. 6a, the increase in the tensile strength of the sediment from 0.9 to 1.4 kPa on the 14th day of exposure we influenced by the content of the components of the organo-mineral complex, namely:
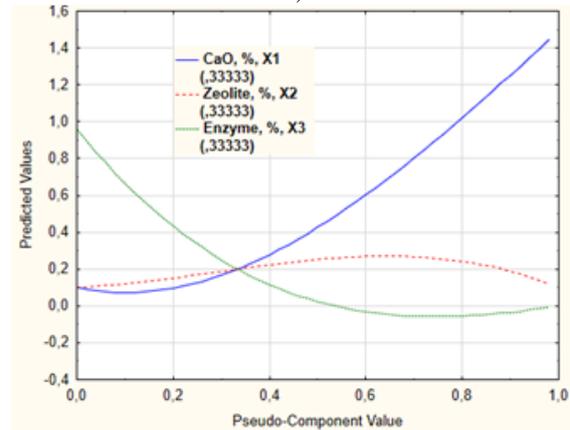
quicklime (*X1*) from 26.5 to 35%, zeolite (*X2*) from 0 to 8% and enzyme (*X3*) from 0 to 2%.
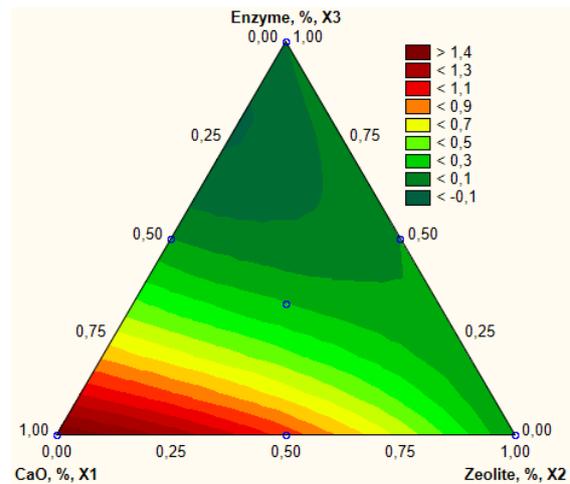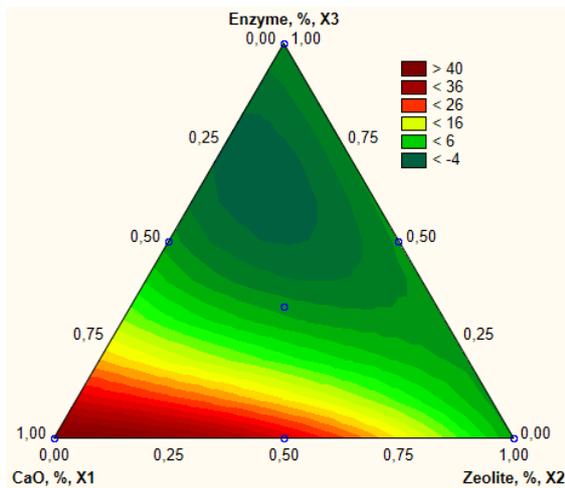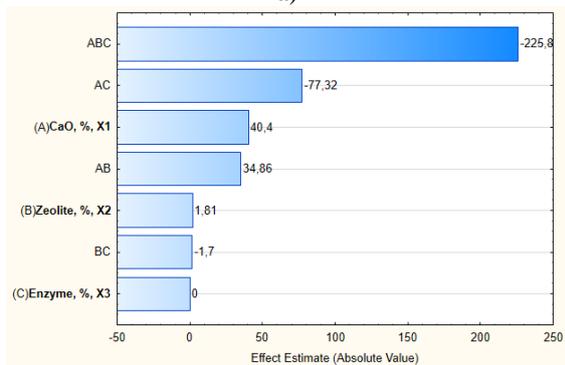

a)
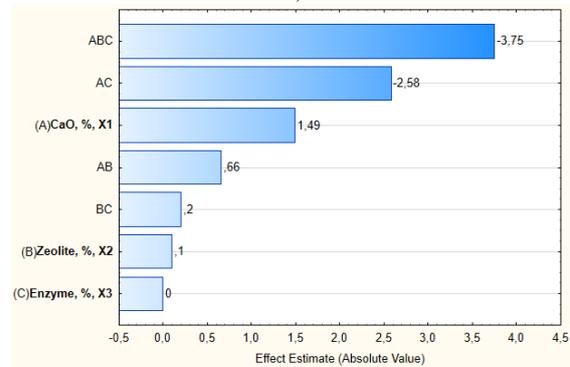
b)

c)

Figure 6 - Ternary surface (a), Pareto diagram (b) and expected reactions (c) of the influence of organo-mineral complex factors on the tensile strength of sediment after 14 days of aging
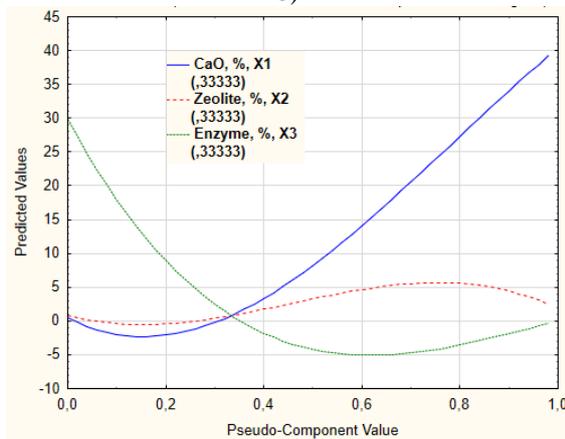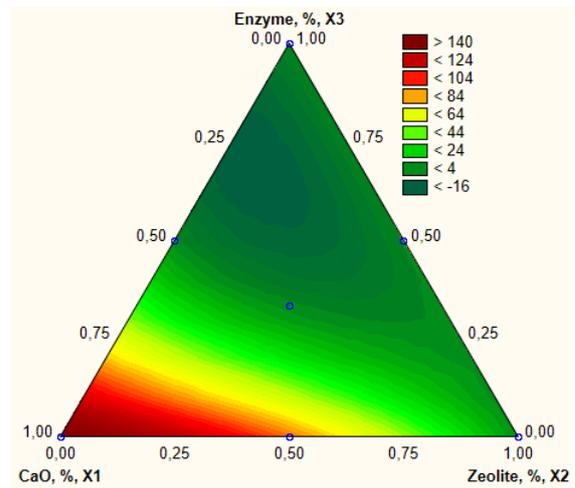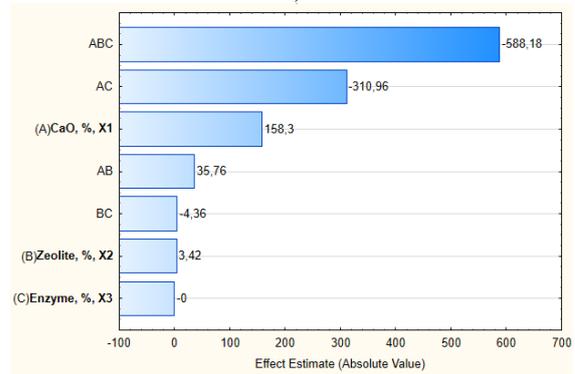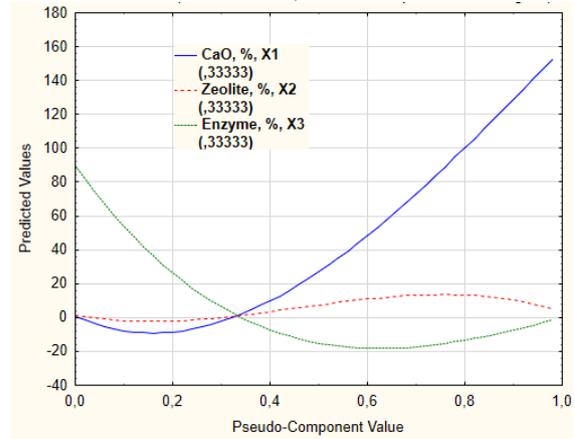
As shown in Fig. 7a, the increase in the tensile strength of the sediment from 16 to 40 kPa after 21 days of aging depends on the content of quicklime (*X1*), which ranges from 27 to 35%; the content of zeolite (*X2*), which ranges from 0 to 8.25%; and enzyme content (*X3*), which ranges from 0 to 2%.

a)

b)

c)

Figure 7 - Ternary surface (a), Pareto diagram (b) and expected reactions (c) of the influence of organo-mineral complex factors on the tensile strength of sediment after 21 days of aging

a)

b)

c)

Figure 8 - Ternary surface (a), Pareto diagram (b) and expected reactions (c) of the influence of organo-mineral complex factors on the tensile strength of sediment after 28 days of aging

As shown in Fig. 8a, the increase in the tensile strength of the sediment from 104 to 140 kPa after 28 days of aging depends on the content of quicklime ($X1$), which ranges from 28.5 to 35%; the zeolite content ($X2$), which ranges from 0 to 6.5%; and the enzyme content ($X3$), which ranges from 0 to 1.6%.

By superimposing ternary surfaces on each other (taking into account the criterion value of the tensile strength of the sediment (Ts→max)), the optimal range of the component composition of the organo-mineral complex was determined. The range is limited along the $X1$ axis by the amount of quicklime from 30.63 to 35%, along the $X2$ axis by the amount of zeolite from 0 to 3.75%, and along the $X3$ axis by the amount of enzyme from 0 to 1.25% (Fig. 9).
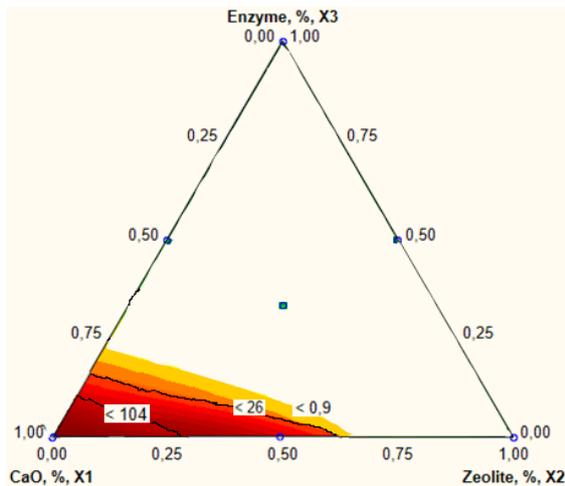
Figure 9 – Combined diagram showing the influence of factors affecting the organo-mineral complex on changes in the tensile strength of sediment

The composition of the organo-mineral complex in a specific area ensures the formation of sediment with a tensile strength of 160 kPa.

Conclusions.

Experimental and statistical modelling was use to determine the optimal organic-mineral composition for removing turbidity and forming mechanically stable sediments. We achieved clear water (up to 1.55 NTU) using a mixture containing 7.25-8.25% quicklime, 2.5-3% zeolite, and 7.5-8.25% enzyme. Sediments with a tensile strength of up to 160 kPa after 28 days we obtained using a mixture containing 30.63–35% quicklime, 0-3.75% zeolite, and 0-1.25% enzyme. The resulting sediment is self-compacting, waterproof, and can be use to construct embankments for storage ponds at solid waste landfills during their recultivation and reconstruction.

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Гузій С.Г.*
Державна установа «Інститут геохімії навколишнього середовища» НАН України
https://orcid.org/0009-0009-4635-2806

Товмаченко А.В.
Державна установа «Інститут геохімії навколишнього середовища» НАН України
https://orcid.org/0000-0002-0674-8410

Вітер В.М.
Державна установа «Інститут геохімії навколишнього середовища» НАН України
https://orcid.org/0009-0005-2551-949

Моделювання органо-мінеральних комплексів у системі "Вапно-цеоліт-фермент" для очищення технічно забруднених вод від зависі та ущільнення осаду

Аннотація. У статті представлено результати експериментально-статистичного моделювання по визначенню оптимальних складів органо-мінерального комплексів для очищення очищення технічно забруднених вод від зависі та ущільнення осаду накопичувальних ставків на звалищах твердих відходів під час їх рекультивації та реконструкції. Прозорість води з показником каламутності 1.55 NTU забезпечується при використанні органо-мінерального комплексу, що містить негашеного вапна в кількості 7.25-8.25%, цеоліту в кількості 2.5-3% і ензиму в кількості 7.5-8.25%. Осадження зависі у вигляді осаду з пластичною міцністю до 160 кПа на 28 добу витримки забезпечується при використанні органо-мінерального комплексу, що містить негашеного вапна в кількості від 30.63-35%, цеоліту в кількості від 0-3.75% і ензиму в кількості 0-1.25%.

Ключові слова: технічно забруднена вода, зависі, каламутність/прозорість, осад, пластична міцність, математичні моделі, оптимізація, органо-мінеральний комплекс, ензим, цеоліт.