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Original Research

Development of environment protection measures based on benthonic clay and sulfuric acid wastes

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Abstract

The oil and gas industry causes man-made changes in all soil components, as well as in water and plants. Crude oil and gas are processed at the same time as the product is produced, and gas condensate and millions of tons of waste are ignored. Recycling oil and gas waste products is essential. Sulfur is widely used in agriculture as a fertilizer and part to fight various plant pests. Soon, not only will the issue of using sulfur dioxide waste as raw materials be solved, but also the problem of contamination of environmental bodies with biological pollutants will be avoided. The use of sulfur-based waste from the oil industry is very effective for antibacterial formulations based on ammonium salts and natural bentonite materials. The developed antibacterial drug can be used to disinfect various facilities. The production tests conducted show the necessity of using the proposed disinfectants to improve the environment. This paste, which includes the proposed bactericidal preparation and bentonite clay in its composition, can be used in veterinary medicine to treat necrobacteriosis in animals. Based on our results, Ammonium sulfate and potassium sulfate obtained from sulfur-containing wastes can be used as fertilizers, and their mixture with bentonite clay can be used as an enhancer in agriculture.

Keywords: Oil industry; Environment; Sulfur; Bentonite; Bactericide

1. Introduction

In recent years, the issue of protecting humans and the environment from the harmful effects of man-made pollution has become increasingly acute, and in this regard, the use of adsorbents has gained special recognition for solving several tasks for the protection of biosphere objects. The most widely used adsorbents are natural clays, which are characterized by chemical resistance, mechanical strength, high ion-exchange selectivity, and a variety of compounds, low cost compared to synthetic organic ion exchangers and other inorganic materials [1]. Bentonite can be attributed to widespread types of clays, which are the result of the decomposition and chemical modification of glassy particles of volcanic ash or tuff [2]. To protect the environment and the integrated use of natural resources, it is necessary to develop and implement low-waste and resource-saving technologies. Development of environmental protection measures based on the use of bentonite clays and sulfur-containing waste disposal products.

To achieve this goal, the following tasks were analyzed:

- Comprehensive study of the material composition, physicochemical, biological, and other properties of bentonite clay from the Urangai deposit of South Kazakhstan region, identification of ways to use it in a mixture with other substances in veterinary practice for therapeutic purposes and for disinfection.
- Technology for processing sulphur-containing industrial waste to produce various commercial products.
- Development of new bactericidal preparations with high bactericidal activity and low corrosion activity.
- Development of environmental protection measures using the bactericidal properties of a mixture of ammonium salts and bentonite clays.
- Development of a method for controlling the content of surfactant alkyl imidazoline in a bactericidal composition.
- Evaluation of the ecological and economic effect of the introduction of bactericidal drugs.

In general, the main idea is to obtain useful products by recycling sulfur-containing waste from various industries and using them in a mixture with bentonite clays to develop environmental protection measures. Further, this research aims to develop new bactericidal formulations with low corrosive and high bactericidal activity compared to the known ones, as well as to establish the possibility of using drugs at subzero temperatures.

2. Methods

The objective of the study is to bentonite clays from the Urangai deposit of the Turkestan region, sulfur-containing waste from the oil industry, and products obtained during their disposal, namely bactericidal preparations used to disinfect livestock complexes, transport facilities, and for the treatment of cattle that are unfavorable for tuberculosis, brucellosis, necrobacteriosis. Potassium and ammonium sulfate are used as fertilizers. The description of the developed spectrophotometric method for analytical control of the content of surfactant alkyl imidazoline used in the work in solutions of a mixture of ammonium persulfate and hydrosulfate salts is explained in several studies [3,4]. The method is based on the well-known principle of enhancing the consistency of the reaction of metal complexation with chromophoric organic reagents cationic surfactants.

To determine alkyl imidazoline, a complex of chromazurol (HAZ) with copper ions was used in the presence of nonionic surfactants – neonol – [5]. The constancy of the pH value (6,0-6,5) was maintained by the urotropine buffer. The determination is hampered by Fe3+, Ni2+, Zn2+ ions in concentrations greater than 0,25; 0,5; 0,5 mg/cm3.The course of the analysis is as follows:

An aliquot amount of the test solution is placed in a 25 ml volumetric flask, then 1 ml of 4,10-3 M copper solution and 0,1% by weight. HAZ, 5 ml of urotropine buffer, and 5 ml of nonionic surfactant solution are added and diluted with water to the mark. The solution is stirred, and after 15 minutes the optical density is determined at 620 nm using 1 cm thick cuvettes relative to the reference solution containing all reagents except alkyl imidazoline. The content of alkyl imidazoline (AIZ) is calculated according to a calibration schedule constructed under the conditions of analysis.

Beer's law is performed in the range of 0,5-8 mg of AIZ in 25 ml of solution. The correctness of the methodology was assessed using the "introduced–found" method. Thus, conditions have been found for the analytical determination of alkyl imidazoline by the spectrophotometric method using the four-component Si-HAZ-AIZ-neonol complex. The technique developed can serve as a method for controlling the content of AIZ in solutions of the drug "Bactericide”. Comprehensive studies have established the structural and sorption characteristics of bentonite clay from the Urangai deposit and revealed its high adsorption capacity during thermal and acid activation due to changes in the acidic properties of the surface.

A technological scheme for the complex processing of sulfur–containing waste is known, which allows one to obtain several valuable commodity products:

- ammonium and potassium sulfates,
- persulfate, hydrosulfate, and
- ammonium thiosulfate.

The synthesis of ammonium salts (sulfate, hydrosulfate, and persulfate) is carried out by the following successive transformations:

$$S_2\,(H_2S) \xrightarrow{O_2} SO_2 \xrightarrow{O_2 + H_2O} H_2SO_4 \xrightarrow{NH_3} (NH_4)_2SO_4 \xrightarrow{H_2SO_4} NH_4HSO_4 \quad (1)$$

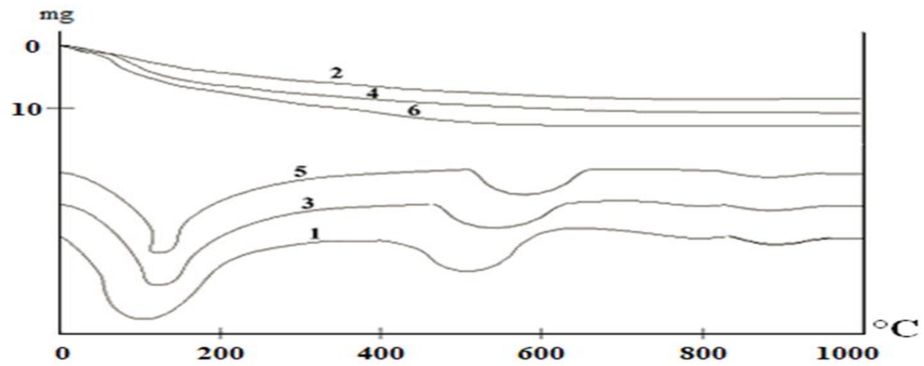
$$(NH_4)_2\,SO_4 \xrightarrow{electrolysis} (NH_4)_2S_2O_8 \quad (2)$$

$$Na_2S_2O_3 + 2HCI = 2NaCI + H_2S_2O_3 \begin{cases} \nearrow H_2SO_3 \\ \searrow S \end{cases} \quad (3)$$

The adsorption of vapors from nitrogen–containing organic base, pyridine (C5H5N), were analyzed to assess changes in surface properties and porous structure, as well as the energy heterogeneity of micropores of bentonite clay, protocols presented in the cited papers [6,7]. When obtaining ammonium hydrosulfate or persulfate, sodium thiosulfate from sulfur, its purification from hydrogen sulfide and mercaptans is not required, since parallel to the oxidation of sulfur, the oxidation of these concomitant substances to sulfurous anhydride proceeds, as presented in the cited papers [8,9].
The physicochemical properties of bentonite after heat treatment and acid activation were characterized by IR spectroscopy, X-ray, and thermography methods. Based on the analysis of derivatograms and thermograms of the initial and activated samples of bentonite clay, three endothermic effects were produced, as seen in Fig.1.

3. Results and discussion

A sufficiently deep endothermic minimum was detected within temperatures above 100-1700C, which corresponds to the release of interpack water (Fig.1). From 1700C to 5000C, this process slows down, and then the endothermic effect reappears (up to 6200C), which indicates the decomposition of hydroxyl groups in the structure and the appearance of anhydrous modification (Fig.2). At 800-900 0C, an endothermic minimum is observed, which may be due to the destruction of the anhydrous modification of montmorillonite



1, 2 – original clay; 3,4 and 5,6 – activated 5% and 25% H_2SO_4, respectively

Figure 1. Derivatograms (1,3,5) and mass loss curves of bentonite clay (2,4,6) at different temperatures

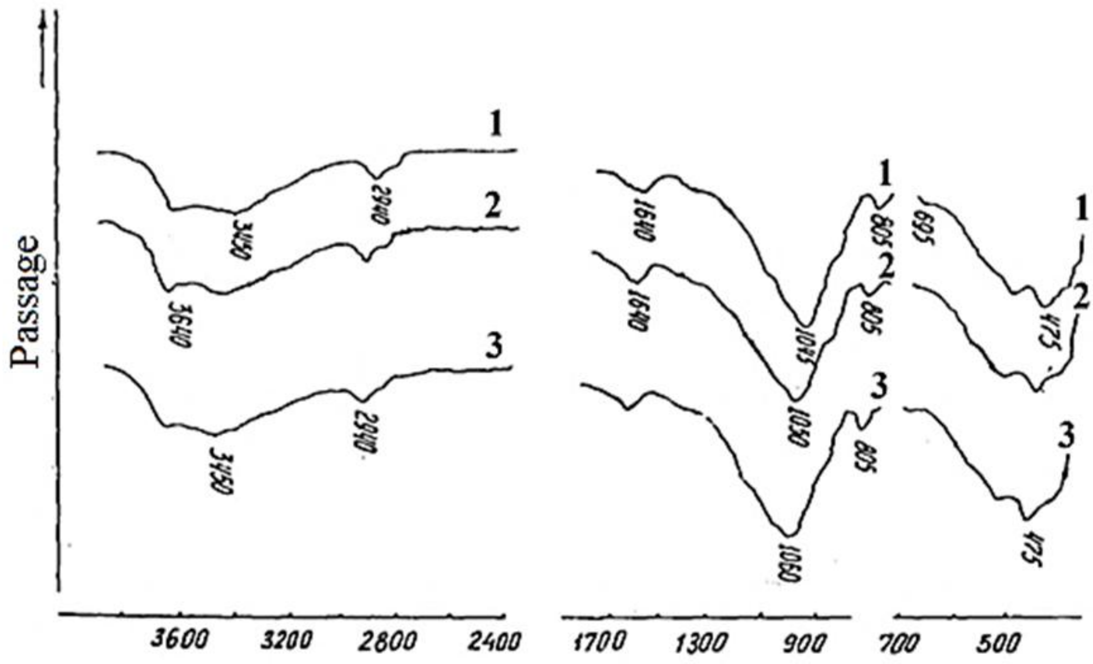


Figure 2. IR spectra of natural (1) and activated 5% (2), 25% (3) solutions of H_2SO_4 bentonite clay.

The results of physicochemical methods, i.e. the observed changes in IR spectroscopy and derivatograms, as well as chemical analysis data (Table 1) indicate the destruction of a clay mineral during activation, including profound changes in its structure.

Table 1. Chemical composition of Urangai bentonite before (1) and after activation of 25% H_2SO_4 (2).

№	Components, %								
	Na_2O	SiO_2	MgO	CaO	K_2O	Fe_2O_3	Al_2O_3	Absorption bands	The amount
1	1,2	58,0	3,7	6,9	0,8	7,0	11,9	10,7	100,2
2	0,32	73,9	1,82	3,8	0,7	2,44	7,0	9,3	99,29

The obtained adsorption isotherms have an S-shaped shape, and their analysis allows us to judge the improvement of the adsorption properties of bentonite both during acidic and thermal activation because of the destruction of the crystal structure of the montmorillonite mineral due to dehydration, decatenation, and an increase in strongly acidic centers. The partial destruction of the crystal lattice of the montmorillonite mineral during thermal activation is evidenced by a noticeable decrease in iron, magnesium, aluminum oxide, alkaline, and alkaline earth metals in samples and an increase in the amount of silica gel. A well-known fact in medicine is the use of $Na_2S_2O_3$ thiosulfate for allergies, arthritis, and neuralgia, for the treatment of scabies caused by ticks and other diseases. When the skin is treated sequentially with a thiosulfate solution, and then with a hydrochloric acid solution, colloidal sulfur is released that destroys parasites.

Based on a comprehensive analysis of the literature data and the results of experimental work, we have found new applications for ammonium salts: we have created a new disinfectant "Bactericide", which is a mixture of persulfate, ammonium hydrosulfate, and alkylimidazoline surfactant, as well as a paste-like mixture "Bentactive", which includes bentonite clay in addition to ammonium salts.

The section considers the possibility of synthesizing ammonium salts (sulfate, hydrosulfate, persulfate), sodium thiosulfate, and potassium sulfate from sulfur-containing waste from the oil industry (Fig. 3) shows a technological scheme for processing sulfur to produce commercial products.

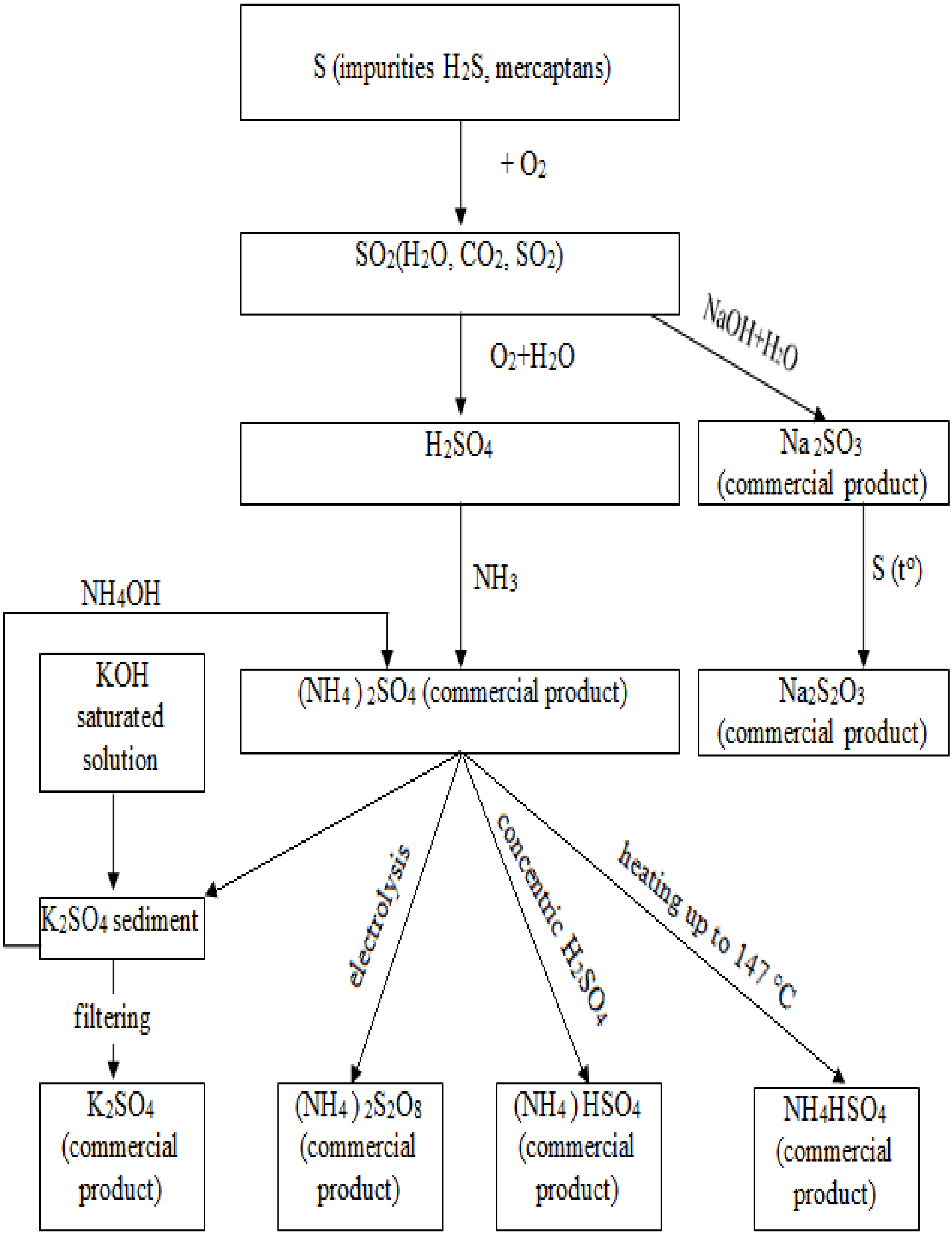
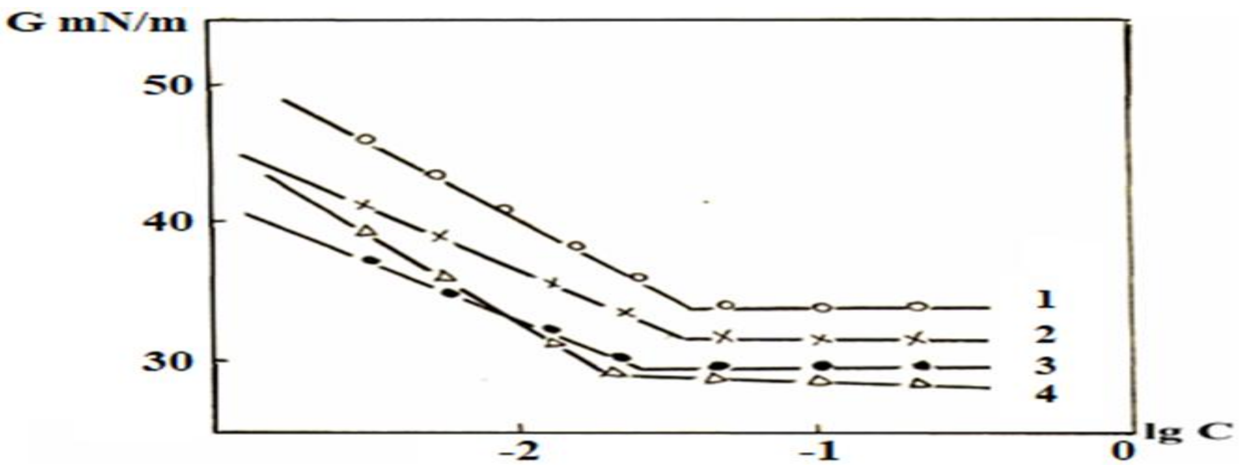


Figure 3. Technological scheme of the sulfur waste processing oil and gas industry with the production of inorganic salts

The increased bactericidal activity of a mixture of persulfate and ammonium hydrosulfate against *Staphylococcus aureus* and other cultures is shown in several studies [10].

The adsorption capacity of alkylimidazoline in salt solutions is higher than in water (Fig. 4). For example, the critical concentration of micelle formation for water is 34,6 mN/m, for "Bactericide", %: 0,1 – 34,4 mN/m; 1.0 – 28,6 mN/m; 5 – 28,0 mN/m, indicating an increase in the surface activity of the surfactant mixture studied.



1-3 - 1% Bactericide – air; 4 - 5% Bactericide – air

Figure 4. Isotherm of the surface tension of the solution alkyl imidazoline at the interface / 298 K/

Experimental data conducted to establish the possibility of using the developed preparations for disinfection of unheated facilities in winter are shown in Fig. 5.

With an increase in the concentration of the drug "Bactericide" in the solution, a decrease in their freezing temperature is observed. For example, a 0,5% solution has a freezing point of -12,8 °C and a 7,0% solution has a freezing point of -14,4 °C. As the results of the experimental values have shown, the bactericidal properties of the drug are preserved at subzero temperatures, which is one of its advantages over other known disinfectants, solutions of which freeze at temperatures below -5 °C.

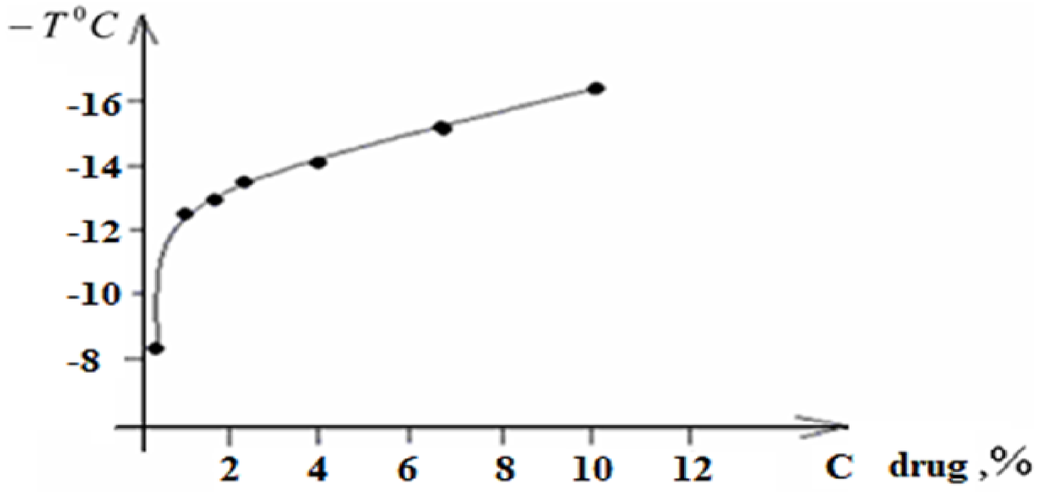


Figure 5. Dependence of the freezing point of aqueous solutions of the drug "Bactericide" on its concentration.

The bactericidal effect of the drug "Bactericide" is based on a violation of the normal course of redox processes in microorganisms that cause their death. Ammonium persulfate acts as an oxidizer, hydrosulfate is used to create an environment for the redox process, and surfactants-alkylimidazoline are chemically compatible with the active substance, inhibit corrosion processes, and increase the bactericidal activity of the drug [11,12].
For disinfection, 0,1-5,0% aqueous solutions of the drug "Bactericide" are used at its consumption in the form of an aerosol of 0.3 l / m2 and in the form of a solution of 0,5 l/m^2 and an exposure of 30 minutes. When the solution is used as a paste, the mass ratios of the components are of the same order. The proposed drugs are harmless from a dermatological point of view, and have a low toxic effect, LD50 for white mice (intragastric) is 983 mg/kg (for "Bactericide") and 755 mg/kg (for "Bentactive") live weight.

Table 2. Characteristics of the bactericidal properties of the drug "Bactericide" (exposure 25 min.).

Ratio $(NH_4)_2S_2O_8$ NH_4HS+ surfactants	Disinfectant concentration, % by weight.	The presence of mycobacterium tuberculosis growth	The presence of brucella growth	The presence of Staphylococcus aureus growth
1 : 1 : 0,005	5,0	- - - -	- - - -	- - - -
	4,0	- - - -	- - - -	- - - -
	3,5	- - - -	- - - -	- - - -
	3,0	- + + -	- - - -	- - - -
	1,0	+ + + +	- - - -	- - - -
	0,5	+ + + +	- - - -	- - - -
	0,1	+ + + +	- + - +	- - - -
	0,05	+ + + +	+ + + +	+ - - +
1 : 2 : 0,005	5,0	- - - -	- - - -	- - - -
	4,0	- - - -	- - - -	- - - -
	3,5	- - - -	- - - -	- - - -
	3,0	- - - +	- - - -	- - - -
	1,0	+ + + -	- - - -	- - - -
	0,5	+ + + +	- - - -	- - - -
	0,1	+ + + +	- - + -	- - - -
	0,05	+ + + +	+ + - -	- - - +
1 : 3 : 0,01	5,0	- - - -	- - - -	- - - -
	4,0	- - - -	- - - -	- - - -
	3,5	- - - -	- - - -	- - - -
	3,0	- + - -	- - - -	- - - -
	1,0	+ + + -	- - - -	- - - -
	0,5	+ + + +	- - - -	- - - -
	0,1	+ + + +	- + + -	- - - -
	0,05	+ + + +	+ + + +	- + - -
Control		+ + + +	+ + + +	

Note: - lack of bacterial growth; + the presence of bacterial growth.

According to the results of tests in various livestock farms, the preparations "Bactericide" and "Bentactive" are recommended, respectively, as disinfectants for the sanitation of various facilities unfavorable for tuberculosis, brucellosis and for the local treatment and prevention of Necrobacteriosis, Psoriasis of farm animals (Table 3).

It follows from the data given in Tables 3-4 that the solutions containing ≥ 0.1% of the drug have 100% disinfecting activity against the culture of Staphylococcus aureus. Regarding mycobacterium culture (tuberculosis), solutions with a concentration of ≥ 3.5% have similar activity, with respect to brucella culture ≥ 0.5%, and necroforum ≥ 3.0% of the drug.

Table 3. Decontaminating activity of the drug "Bentactive" (concentration according to active substance-3.0% by weight, exposure -1.5 hours, consumption 0.5 l /m^2)

The form of disinfectant used	The presence of necroforum growth on the nutrient medium MPA								
	Tree	Con-crete	Brick	Tiles	Iron	Steel	Alumi-num	Rubber	Glass
With organic protection									
Solution	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -
Pasta	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -
Without organic protection									
Solution	- - - -	- - - -	- - - -	- - - -	- - - -	- - --	- - - -	- - - -	- - - -
Pasta	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -
Control	++++	++++	++++	++++	++++	++++	++++	++++	++++

The developed preparations meet modern disinfectants requirements, have sufficiently high bactericidal effects, are odorless, dissolve well in water, are transportable, and decompose in the external environment without residues harmful to the environment. This development makes it possible to replace poorly available and toxic drugs used in animal husbandry to destroy tuberculosis, and Brucellosis pathogens in the external environment, such as alkaline and chlorinated cresols, phenol, formalin, and its mixtures with creolin, glutaraldehyde, caustic and soda ash, peracetic acid, lime chloride, sodium hypochloride, and others. As observed in table 4, the drug "Bactericide" is less corrosive.

The combination of the drug "Bactericide" with bentonite clay, called "Bentactive", allowed one to obtain a composition with not only increased bactericidal activity (Table 4), but also a washing and tanning effect on a tissue surface prone to purulent necrotic decay.

Table 4. Comparative data on the corrosive effect of various preparations on aluminum

№	The composition of drugs, mass. %	Corrosion rate, g/m^2. day.	Comparative effectiveness of corrosion protection	
			NaOH	Na_2CO_3
1	2% NaOH	0,138	-	-
2	2% Na_2CO_3	0,149	-	-
3	5% [NH_4HSO_4 + $(NH_4)_2S_2O_8$]	0,023	6,0	6,5
4	5% [NH_4HSO_4 + $(NH_4)_2S_2O_8$] + 0,02 % alkylimidazoline	0,009	15,3	16,6
5	5% [NH_4HSO_4 + $(NH_4)_2S_2O_8$] + 0,2 % alkylimidazoline	0,007	19,7	21,3
6	5% [NH_4HSO_4 + $(NH_4)_2S_2O_8$] + 0,5 % alkylimidazoline	0,003	46,0	49,7
7	5% [NH_4HSO_4 + $(NH_4)_2S_2O_8$] + 0,8 % alkylimidazoline	0,003	46,0	49,7

4. Conclusions

The results of this study were accepted for implementation in production, which confirms the reliability of the main conclusions and provisions. Based on IR spectroscopy, derivatograms, and chemical methods, changes in both the composition and surface and structural properties of bentonite clay were established during activation using acids and high temperatures. For the first time, the adsorption of the polar organic substance pyridine on the initial bentonite clay, as well as on thermo-activated and acid-activated bentonite clay of the Urangai deposit, was presented. During thermal activation, the adsorption capacity of bentonite clay increases by 40% due to dehydration and destruction of the crystal structure. Based on the results of theoretical and experimental studies, the possibility of processing sulfur waste from the oil industry to produce several commercial products – ammonium and potassium sulfates, persulfate, hydrosulfate, and ammonium thiosulfate has been established. The high bactericidal activity of a mixture called "Bactericide" consisting of persulfate, hydrosulfate, and alkylimidazoline was revealed, and the possibility of its use for disinfection of objects unfavorable for tuberculosis, brucellosis, necrobacteriosis, and other infectious diseases was shown. The possibility of using a paste-like composition of Bentactive, including bentonite clay and the drug bactericide for the treatment of cattle necrobacteriosis is presented. Finaly, a new method for the determination of surfactant alkylimidazoline in disinfecting saline solutions has been developed.

Declaration of Competing Interest

The authors declare that they have no known financial or non-financial competing interests in any material discussed in this paper.

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References

[1] Alinia-Ahandani, Ebrahim, Zahra Alizadeh-Terepoei, and Ani Boghozian. "Positive role of green tea as an anti-cancer biomedical source in Iran northern." *Am J Biomed Sci Res*, 5, no. 1,15-8,2019.

[2] Kianersi, Ali, Mastaneh Hajipour, and Ebrahim Biniaz Delijani. "Experimental evaluation of bentonite clay swelling and inhibition effect of nanoparticles." *Environmental Earth Sciences*, 82, no. 22 ,526, 2023.

[3] Sheydaei, Milad, and Ebrahim Alinia-Ahandani. "Synthesis and characterization of methylene-xylene-based polysulfide block-copolymer/carbon nanotube nanocomposites via in situ polymerization method." *Journal of Sulfur Chemistry,* 41, no. 4, 421-43, 2020.

[4] Lotfipour, Farzaneh, Morteza Milani, Mohammad Reza Nahaei, Vahid Javaherzadeh, Amin Omrani, and Navid Attar. "Antibacterial Activity of Germicide-P®: A Persulfate Based Detergent/Disinfectant on Some Hospital Isolates: Antibacterial activity of germicide-P." *Iranian Journal of Pharmaceutical Sciences* 2, no. 4, 225-230,2006.

[5] Shilykovskaya, D. O., S. A. Denisova, and A. M. Yelokhov. "A Study of the Solubility and Extraction Capacity of Systems Based on Mixtures of Neonols AF 9-6 and AF 9-12." *Polymer Science, Series D*, 16, no. 3, 567-571,2023.

[6] Chellapandi, Thangapandi, and Gunabalan Madhumitha. "Montmorillonite clay-based heterogenous catalyst for the synthesis of nitrogen heterocycle organic moieties: A review." *Molecular Diversity*, 26, no. 4, 2311-2339, 2022.

[7] Kumar, P. Vinoth, and G. Madhumitha. "Clay based heterogeneous catalysts for carbon–nitrogen bond formation: a review." *RSC advances*, 14, no. 7,4810-4834, 2024.

[8] Chan, Yi Herng, Adrian Chun Minh Loy, Kin Wai Cheah, Slyvester Yew Wang Chai, Lock Hei Ngu, Bing Shen How, Claudia Li et al. "Hydrogen sulfide (H2S) conversion to hydrogen (H2) and value-added chemicals: Progress, challenges and outlook." *Chemical Engineering Journal* 458, 141398, 2023.

[9] De Angelis, A. "Natural gas removal of hydrogen sulphide and mercaptans." *Applied Catalysis B: Environmental,*113, 37-42, 2012.

[10] Lee, Se-Rim, and Do-Kyun Kim. "Synergistic antimicrobial effects of ammonium persulfate, ultrasound, and mild heat on Staphylococcus aureus under varied conditions." *Food Bioscience,* 62,105406,2024.

[11] Pino, Sam, Shih-Lieh Fang, and Lewis E. Braverman. "Ammonium persulfate: a safe alternative oxidizing reagent for measuring urinary iodine." Clinical chemistry 42, no. 2, 239-243,1996.

[12] Li, Nianyin, Jing He, Pingli Liu, Qian Zhang, Ying Xiong, Xingde Zhang, Qiang Wang, Yu Kang, and Chao Ma. "Research progress of corrosion inhibitors for high-temperature hydrochloric acid acidification." *Corrosion Reviews*, 42, no. 6, 703-725, 2024.