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Development and Investigation of Hydrogen Sulfide Adsorbents From Natural Materials

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Abstract. Adsorption materials based on natural minerals are considered in the world literature as inexpensive hydrogen sulfide adsorbents capable of completely replacing commercial products such as synthetic zeolites. The global demand for inexpensive, accessible, safe materials is growing, including in the field of cleaning industrial and agricultural gas emissions from hydrogen sulfide. The article presents an analysis of literary data on natural clays, activated sludge and other materials and methods of their use for hydrogen sulfide adsorption. Data on the composition of activated sludge, clays and limestone rocks are provided. The composition studies were carried out on an infrared spectrophotometer. The inorganic component of activated sludge includes iron oxide, aluminum, calcium, magnesium compounds, and silicates. Limestone consists of carbonates, iron oxide, silicates, and when calcined at high temperatures, it mainly forms calcium oxide. Various clays contain aluminosilicates, iron oxides, copper, cobalt, and manganese. Due to the content of metal oxides, natural materials have a chemisorption mechanism, and due to the content of aluminum and silicon compounds, they have a physical sorption mechanism. 17 compositions of composite materials from natural minerals were developed and their sulfur content was studied. A study was also conducted on the absorption capacity of activated sludge in a liquid state. It was shown that all natural materials have a high potential for use as adsorbents with minimal preparation (dehydration, calcination). Compositions that do not contain expensive additives, consisting mainly of calcined limestone rock and clays, showed sulfur capacity from 10 to 40 %.

Key words: hydrogen sulfide, adsorbents, clay, bentonite, limestone, gas purification

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Разработка и исследование адсорбентов сероводорода из природных материалов

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Реферат. Адсорбционные материалы на основе природных минералов рассматриваются в мировой литературе как недорогие адсорбенты сероводорода, способные полностью заменить

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коммерческие продукты, такие как синтетические цеолиты. Мировой спрос на недорогие, доступные, безопасные материалы растет, в том числе в сфере очистки промышленных и сельскохозяйственных газовых выбросов от сероводорода. В статье представлен анализ литературных данных о природных глинах, активном иле и других материалах и способах их использования для адсорбции сероводорода. Приведены данные о составах активного ила, глин и известняковых пород, исследования которых проведены на инфракрасном спектрофотометре. Неорганическая составляющая активного ила включает в себя оксид железа, соединения алюминия, кальция, магния, силикаты. Горная известковая порода состоит из карбонатов, оксида железа, силикатов, при прокаливании при высоких температурах образует преимущественно оксид кальция. Различные глины содержат алюмосиликаты, оксиды железа, меди, кобальта, марганца. За счет содержания оксидов металлов природные материалы имеют механизм хемосорбции, а за счет содержания соединений алюминия и кремния обладают физическим механизмом сорбции. Разработаны 17 составов композиционных материалов из природных минералов и изучено их содержание серы. Также было проведено исследование поглощающей способности активного ила в жидком состоянии. Показано, что все природные материалы обладают высоким потенциалом для использования в качестве адсорбентов при минимальной подготовке (обезвоживании, прокаливании). Композиции, не содержащие дорогостоящих добавок, состоящие в основном из обожженной известняковой породы и глин, показали сероемкость от 10 до 40 %.

Ключевые слова: сероводород, адсорбенты, глина, бентонит, известняк, очистка газа

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Introduction

The search for the method of removing hydrogen sulfide from gas flows was an urgent problem for several decades [1–2]. This is due to the constant growth of world demand for energy from fossil types of fuel, biofuel, biogas, natural gas and other types of hydrocarbon fuel, which acquires more and more importance in the production of electricity. Cleaning gaseous fuel from hydrogen sulfide is important due to the following reasons: 1) H_2S changes the pH of the atmosphere and participates in the formation of acid rains; 2) hydrogen sulfide is the cause for the appearance of a pungent odor, which affects mainly the urban population near the wastewater treatment plants; 3) H_2S is a toxic gas, it is included in the list of toxic industrial compounds, therefore it is necessary to ensure protection and compliance with safety precautions when working with this gas; 4) there is an increased corrosion activity in relation to equipment, especially in natural gas pipelines or steam boilers; 5) hydrogen sulfide dexactivates catalysts that are used to convert fuel or for various energy processes, for example, in fuel elements.

The separation of hydrogen sulfide from air flows using adsorption is considered as one of the most effective and economical methods. Ensuring environmental stability directed the attention of researchers to the use of natural materials as a source of effective H_2S adsorbents. These materials, subjected to pyrolysis, with additional activation of or without it, were investigated by various authors [3–6]. Good indicators of natural materials during desulfurization were associated not only with superficial alkalinity due to the high content of calcium and magnesium, but also with other components of the inorganic phase of sediment, such as iron or copper compounds that could contribute to oxidation reactions.

A possible alternative to commercial technologies for removing carbon dioxide and other pollutants from biogas is the use of inexpensive natural materials, such as clay, zeolite, fly ash and wood ash. These materials are already used for commercial purposes to purify water, natural gas and in adsorption processes [3] their main advantages include the low cost, availability and simplicity of separation processes. The main restriction of the use of inexpensive natural materials for the purification of biogas is low absorbing ability. However, this process can be improved by activating materials using physical and chemical methods to increase their adsorption ability.

This article considers the use of inexpensive natural and modified materials to remove pollutants from biogas. The purpose of the work is to develop and study the possibility of using various natural materials for the purification of biogas, natural gas and other types of hydrocarbon fuel from hydrogen sulfide. In addition, this study conducted a review of literary data, the advantages and disadvantages of various inexpensive materials used to clean and improve the quality of gaseous fuel containing hydrogen sulfide are considered.

Literature review

Inexpensive materials for the purification of gaseous fuel from hydrogen sulfide include easily accessible and effective natural materials. It is possible to produce adsorbents from local and natural materials that are effective for purifying biogas. Such materials include ash -rich soils, biological activated sludge, coal, clay, rocks, etc. Their use reduces costs as compared to other materials. These materials demonstrated high efficiency, reaching the following indicators: clay (90 %); New Zealand brown soil rich in iron (93.8 %); industrial steel cotton wool (95 %) and compost (80 %) [4]. This study proposes new ways to increase the efficiency of natural materials due to thermal preliminary processing of biomass ash to reduce moisture content, modify the surface of activated coal to improve the absorption of acidic gases, integrate adsorbents to create synergy, regeneration and re -use of adsorbents to increase the environmentalness of the process. The use of natural materials has great prospects in achieving the goals of sustainable development of the United Nations, especially in developing countries.

The economy of the closed cycle concept of implies the use of waste as a secondary raw material as part of a program for renewable and stable energy sources. At wastewater treatment plants, one of the most important waste is activated sludge, and in recent years its disposal has been widely discussed. In [7], wastewater sediment from treatment facilities was used as raw materials for the production of activated coal by the method of physical and chemical activation. The resulting activated carbon was subsequently tested for the removal of hydrogen sulfide in order to further use for deodoration at the wastewater treatment station. The effect of activation temperature and the chemical reagent (NaOH and KOH) in the process of activation were studied. On the one hand, the characteristics of each obtained coal sample were analyzed in terms of surface area according to the BET method (Brunauer–Emmet–Tylor), pore and micropor volume, pore diameter, surface morphology and ground-pot. On the other hand, BET isotherms were also calculated. Finally, both the obtained activated carbon and commercial samples were tested for H_2S removal from the gas flow. The results showed that the optimum temperature of physical and chemical activation is 600 °C and 1000 °C, respectively, and the best of the tested activating substances is KOH. The coal prepared activated carbon showed excellent properties (specific surface area of about 300 m^2/g) for removing H_2S, even higher efficiency than the tested commercial samples of activated coal.

A similar study was presented in [8]. The work analyzed the temperature effect of the activated sludge pyrolysis to obtain coal and the concentration of potassium hydroxide on the desulfurization process. The efficiency of hydrogen sulfide adsorption with activated potassium alkali coal, obtained from activated sludge, was optimal and amounted to 94 %.

Diffusion through active activated sludge as a bio-cleaning system to eliminate odors has been used for more than 30 years, but has limited use due to disagreements in the literature regarding the effect on the efficiency of wastewater treatment [9–12]. Researchers are actively engaged in the use of activated sludge as an adsorbent pollutant [13].

In [14], the authors proposed using activated sludge to clean air from hydrogen sulfide at state treatment facilities. The experiments were carried out on a laboratory installation and it was shown that H_2S in concentrations that usually release during wastewater purification (less than 50 ppm) can be effectively cleaned by diffusion through activated sludge without prejudice to the productivity of the purification process with activated sludge.

In the work [14] it was shown that the use of diffusion through activated sludge as a two -stage wastewater treatment system and elimination odors is an alternative to traditional processes of sulfuric outing gases purification, such as biofilters, bioskrubbers and biosettling tanks, both from a practical point of view (use of existing structures) and from economic (minimal capital costs).

Natural adsorbents gaining popularity in recent years are clay adsorbents, which are relatively new. This class of materials is studied for their adsorption ability due to their prevalence, low cost, stability and environmentally friendly characteristics. Clay minerals, widespread in nature, have unique physical and chemical properties that make them indispensable in many areas, especially for the industrial removal of pollutants from smoke gases. Clay minerals have a unique layered structure, cation-exchange ability, high specific surface area and thermal stability, and are also inexpensive, which makes them promising as adsorbents and carriers of catalysts [15]. The common natural clay minerals mainly include kaolinitis, montmorillonite, bentonite, vermiculite, Illit, sepiolite, saponite, etc. In the review [16], the types and structures of common clay minerals and their methods are presented modifications. It describes the latest achievements in the use of modified clay materials to remove pollutants from flue gases, with an accent to the adsorption ability and mechanism of adsorption of sulfur and volatile organic compounds.

Often used clay adsorbents are kaolinitis, bentonite and palygorskite. Several studies were conducted to compare various types of clay minerals as adsorbents. One of them is the study [16], which used kaolinitis, montmorillonite, palygorskite and vermiculite to remove sulfur compounds from the gas phase. This revealed the differences between clay minerals, despite the fact that vermiculite has a slightly larger surface area, kaolinitis showed better performance compared to other adsorbents due to differences in the mineralogical composition. This emphasizes the effect of differences in the types of adsorbents of clay on their productivity and interaction with sulfur compounds.

Most importantly, clay minerals can be modified to regulate their adsorption ability, and the developed material can be regenerated and used again. Clay minerals can be used as adsorbents of various compounds from the gas phase. However, this topic has not yet been fully studied. There are reports about the use of minerals such as kaolinitis, galluli, montmorillitis, bentonite, saponite, verminculite, illit, sepiolite and palygorskit, for cleaning of a wide range of pollutants, including CO_2, CH_4, SO_2, H_2S, NH_3 and flying organic compounds, such as butylaldegide, oil acid, dimethyldisulfide, n-gexan, benzene, methanol [17].
The latest classification of the studied clay adsorbents is adsorbents based on a metallorganic frame (MOF). They attracted the researchers' attention because of their characteristics, such as a large volume of pores, a designed crystalline structure and an adjustable size of pores. By changing the metal and the organic connecting agent MOF, the size of the pores can be changed [18]. With such strong opportunities, the use of MOF also has disadvantages. It is necessary to establish selectivity according to sulfur so that it becomes a viable adsorbent for desulfurization. MOF also has poor thermal and mechanical stability.

The search of effective adsorbent for desulfurization is constantly ongoing. Since the adsorbents of clay are stable, inexpensive and demonstrate great potential for sulfur adsorption, studies using these materials do not stop. The study [19] shows good bentonite performance for adsorption of more voluminous heterocyclic compounds of sulfur. This offers the idea of using bentonite as an additional process for removing sulfur compounds, which were not completely removed, for example, in the amino cleaning process.

Thus, the removal of H_2S is of primary importance to prevent negative consequences, such as the impact on people and the environment as a whole. It has been shown that natural materials are effective, promising and relatively new candidate material in the H_2S adsorbents. Nevertheless, despite the fact that some technologies are used on an industrial scale, they are far from being perfect. Thus, there is a great potential for their improvement and optimization in order to further reduce costs and increase the characteristics of the separation of gaseous fuels.

Materials and methods

Equipment used in the work:

To analyze the composition of the solid phase of natural materials, IR spectrophotometric analysis was performed on a Shimadzu IRAffinity-1S spectrophotometer.

To determine the adsorption capacity of the studied adsorbents, spectrophotometric detection of sulfides in an absorbing solution of cadmium acetate was used on a Shimadzu UV-1800 UV spectrophotometer at a wavelength of $\lambda = 670$ nm.

Testing of the developed adsorbents from natural materials in laboratory conditions was carried out on a laboratory setup, including a gas source, an adsorbent tube filled with an adsorbent, and a receiver with an absorbent solution.

The following natural materials were used as adsorbents in this work: activated sludge, clays (red, kaolin, bentonite, “Ural” yellow, “Ural” blue, “Uzbek” pink, “Astana” white, “Aktobe” white), limestone rock of the Volga River (Table 1).

Table 1

Appearance of the natural materials used

Name of natural material	Appearance	Name of natural material	Appearance
Natural limestone rock		Clay “Uzbek” blue	
Calcined limestone rock		Clay “Ural” yellow	
Red clay		Clay “Uzbek” pink	
Clay “Aktobe” white		Clay “Astana” white	

Composition and analysis of activated sludge:

Experimental laboratory studies were conducted using excess activated sludge, the species composition of which is represented by biological microorganisms. The structure of activated sludge is a flocculent mass of brown color, which is a heterogeneous system related to fine suspensions. The main organic components are proteins, fats and carbohydrates, which make up 75–85 % of the ash-free (organic) matter. The remaining 15–20 % is accounted for by the lignin-humus complex.

The inorganic component of activated sludge includes hydroxides, phosphates, carbonates, silicates and other compounds.

Some components of the inorganic composition of activated sludge are:

• Quartz (SiO_2).

• Iron compounds in the form of magnetite (Fe_2O_3).

• Aluminum and silicon compounds in the form of muscovite ($(K, Na)Al_2(Si, Al)_4O_{10}(OH)_2$) and illite ($KAl_2(Si_3Al)O_{10}(OH)_2$).

• Calcium and magnesium compounds in the form of phosphates ($Ca_9Fe(PO_4)_7$, $Ca_{18}Mg_2H_2(PO_4)_{14}$, $Ca_9FeH_{0.9}(PO_4)_7$).

The inorganic component of the sludge also includes heavy metal colloids in the form of hydroxides, which arrived in this form from the primary settling tanks [20].

After filtering the liquid portion and drying for two hours at a temperature of 100 °C, the inorganic phase of the activated sludge was analyzed using an IR spectrophotometer (Fig. 1).

Table 2 shows the decoding of IR spectra based on the characteristic absorption bands of certain bonds or groups of atoms.

According to the results of IR spectrophotometry, the inorganic composition of activated sludge is represented mainly by humic substances, namely, fulvic acids. The following intense absorption bands were found in the IR spectra: 3500–3400 cm^{-1}, relate to OH groups (phenolic, alcohol and OH groups in carboxyl groups); 2923 cm^{-1} – indicates the presence of long methylene chains; 2852 cm^{-1} – relates to methyl end groups. The absorption band at a wavelength of 1714 cm^{-1} corresponds to carboxyl groups (C=O in carboxyl groups), 1651 cm^{-1} – C=N in imino groups. 1452 cm^{-1} corresponds to methyl and methylene groups, 1204 cm^{-1} – OH groups in carboxyl groups, 1105 cm^{-1} – OH groups of carbohydrates. The IR spectra of fulvic acids also contain absorption bands with an intensity of 2928 and 1500 cm^{-1}, which correspond to CH_2-, CH_3-groups and C=C (arom). Strong absorption in the region of 1100 cm^{-1} is associated with deformation vibrations of OH-alcohol groups. Such a spectrum is characteristic of fulvic acids, which contain less nitrogen and carbon, and more oxygen and hydrogen, compared to humic acids.

Composition and analysis of the Volga River limestone rock:

Limestone rock is a crumbly inorganic material, white with yellow and light brown inclusions. Since most of the limestone rock is calcium carbonate, when heated (over 840 °C), it decomposes with the release of carbon dioxide and calcium oxide (quicklime). Fig. 2 and 3 show the spectra of limestone rock before and after pyrolysis.

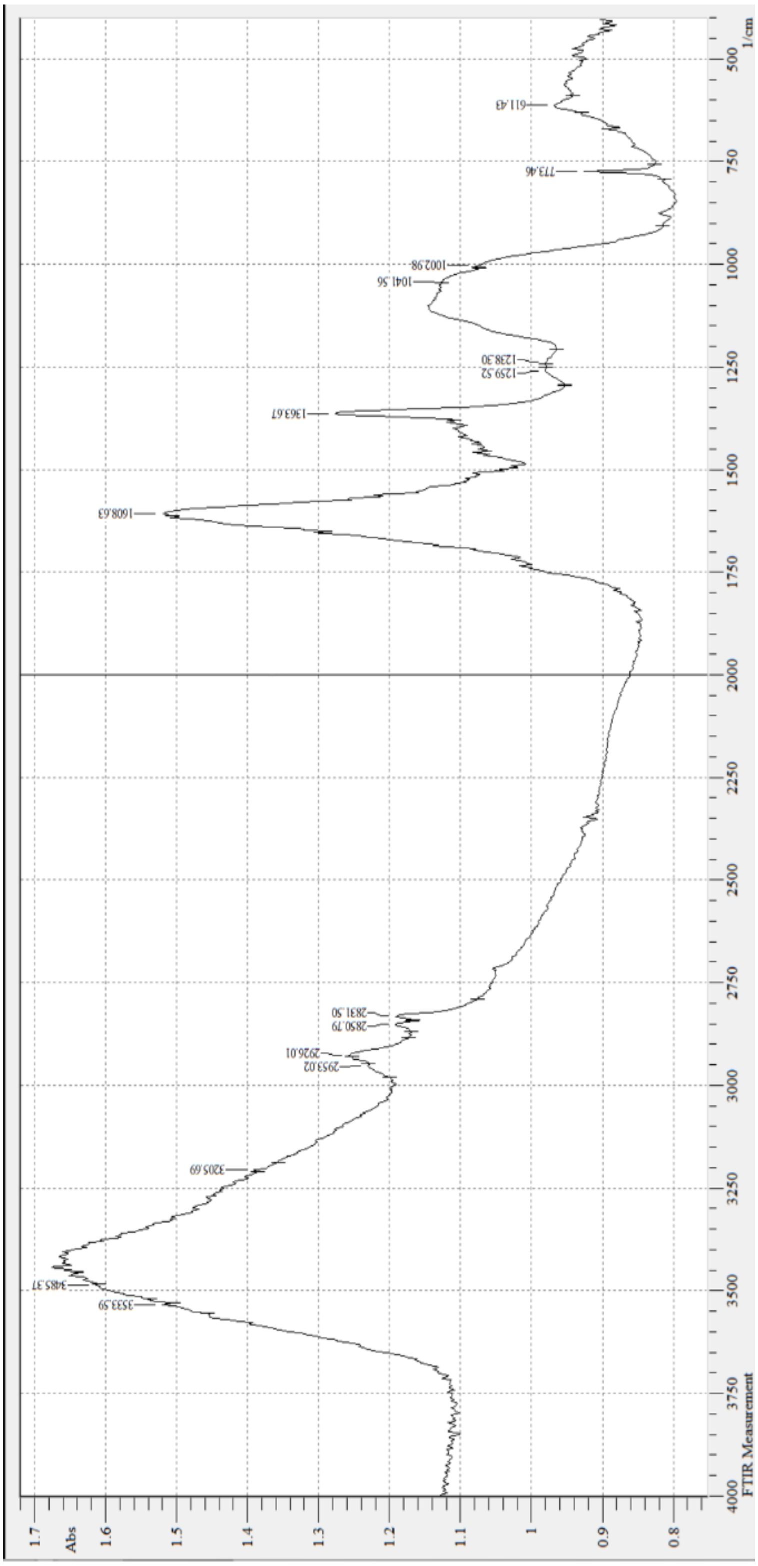

Fig. 1. IR spectrum of activated sludge

Table 2

Table of characteristic frequencies for the IR spectrum of activated sludge

Absorption range, cm^{-1}	Activated sludge
3500	valence O-H groups
2950	valence bonds of alkanes
2815	valence C-H groups
2700	valence O-H bonds of carboxylic acids
2325	CO_2 from the atmosphere and aliphatic groups of carboxylic acids
1750	C=O bonds
1651	C=N bonds in imino groups
1600	valence conjugated and benzene bonds
1500	small amount of aromatic compounds
1355	valence C-H groups
1250	carboxylic acid groups COOH and C-C bonds
1100	sulfates, alcohols, ethers
1040	characteristic peaks for humic substances
1000	silicates
870	carbonates
750	silicates
620	sulfates
611	characteristic peaks for humic substances
500	iron oxide, silicates

Table 3 shows the decoding of IR spectra based on the characteristic absorption bands of certain bonds or groups of atoms.

The results of IR spectroscopy showed that limestone rock has good potential for capturing hydrogen sulfide, especially after preliminary heat treatment, due to the content of predominantly alkaline earth metal oxides in its composition.

Composition and analysis of clay materials:

Table 4 presents compositions of the inorganic part of various types of clays.

The chemical composition of clay materials can simultaneously provide strength of adsorbents due to the high content of silicon and aluminum oxide, porosity due to the finely dispersed composition, and chemisorption due to compounds of iron, copper, cobalt, chromium, cadmium, and manganese.

Preparation of composite adsorbents from natural materials:

Natural materials (activated sludge, clays, limestone rock) after preliminary preparation were mixed in certain proportions with sodium alkali, water, zinc oxide, iron, copper, manganese, extrudates were obtained with an average granule surface area of 50 mm^2, dried for 1 hour at a temperature of 100 °C. Preliminary preparation of activated sludge consisted of filtering the liquid part and drying for two hours at a temperature of 100 °C. Preliminary preparation of limestone rock consisted of pyrolysis at 1000 C° for 2 hours. Clays were not pretreated in any way.

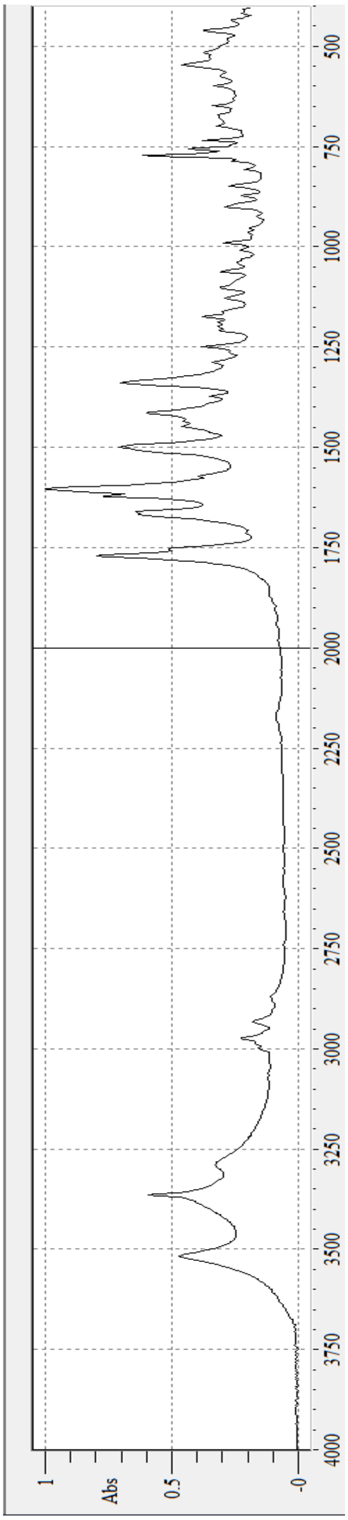

Fig. 2. IR spectrum of limestone rock

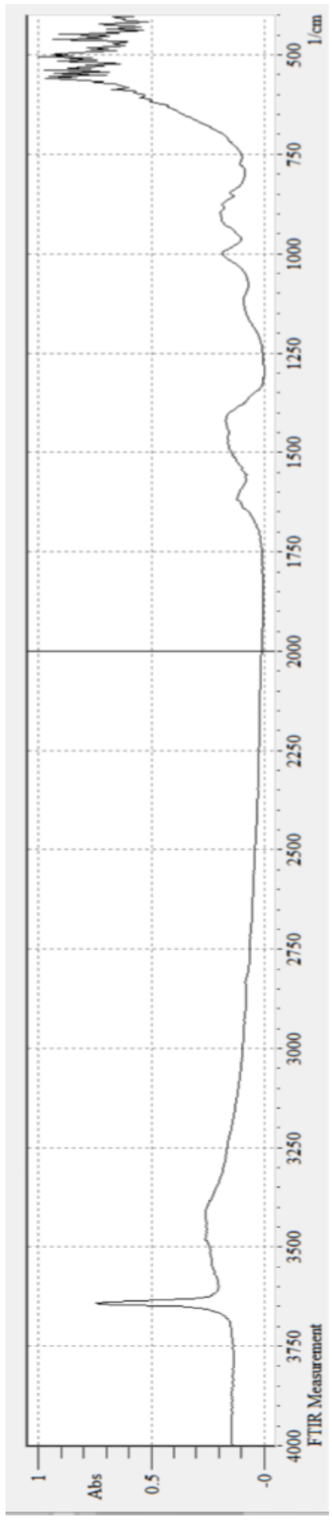

Fig. 3. IR spectrum of limestone rock after pyrolysis at 1000 °C for 2 hours

Table 3

Table of characteristic frequencies for IR spectra of limestone rock

Absorption range, cm^{-1}	Natural	After pyrolysis
3640	valence OH bonds $Ca(OH)_2$ – the main component	valence OH bonds $Ca(OH)_2$ – the main component
3500–3400	valence OH groups	valence OH groups with hydrogen bonds
3360	valence CH bonds	valence CH bonds
3350	stretching vibrations of the NH group – organic residues – amino acids, proteins in large quantities	–
3250	iron oxide	iron oxide
3210	valence C=N–H bonds	valence C=N–H bonds
2950	valence bonds of alkanes	–
2850	valence C-H groups	–
2833–2750	CHO-aldehydes, OCH_3-esters, aromatic compounds in large quantities	stretching vibrations of the aldehyde group CHO
2325	CO_2 from the atmosphere and aliphatic groups of carboxylic acids	–
1700	C=O bonds – unsaturated and aromatic aldehydes and ketones in large quantities	–
1600	inorganic calcium, gypsum, quartz, clay, dolomite	unburned carbon-like organic compounds and bound water
1450	condensed aromatic benzene rings	
1414	calcium carbonate	calcium oxide
1280	ethers	–
1100	sulfates	sulfates and brown soil
1000	silicates	silicates
997.2	deformation vibrations of $CH=CH_2$ bonds – unsaturated hydrocarbons	–
950	clays	clays
870	carbonates	carbonates
848	aromatic compounds	–
750–774	silicates	silicates
620	sulfates	sulfates, brown soil, clays, silicates
500	iron oxide, silicates	iron oxide, silicates

Table 4

Characteristic chemical components in the composition of clays

Name	Chemical composition providing the main properties
Bentonite	Montmorillonite $Al_2[Si_4O_{10}](OH)_2 \cdot nH_2O$
Kaolin	Kaolinite $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$
Red clay	Fe_2O_3, MnO
Blue clay	Co^{2+}, Cd^{2+}
Pink clay	Al_2O_3
Yellow clay	CuO, Fe_2O_3
White clay	$CaCO_3$

The calculation of sulfur capacity was carried out using the formula

$$A,\% = \left[\frac{\left(\frac{(C_0 - C) \cdot n}{m} \right)}{1000} \right] \cdot 100\,\%,$$

where C_0 – initial concentration, mg; C – residual concentration, mg; n – the proportion of adsorbate that enters the collecting solution; m – adsorbent mass, g.

Results

The composition and characteristics of the obtained adsorbents from natural materials are presented in Table 5. The compositions are arranged in order of increasing sulfur capacity.

Table 5

Component composition of the developed adsorption materials and measured sulfur capacity

N	Composition of the adsorbent	Sulfur capacity, %
1	10 % bentonite, 74.7 % ZnO, 15.3 % NaOH	0
3	10 % natural rock, 15.3 % NaOH, 74.7 % ZnO	0
4	10 % kaolin, 74.7 % ZnO, 15.3 % NaOH	0
5	50 % bentonite, 8.5 % NaOH, 41.5 % Fe_2O_3	0
6	50 % kaolin, 8.5 % NaOH, 41.5 % Fe_2O_3	0.9
7	50 % calcined rock, 8.5 % NaOH, 41.5 % Uzbek clay (pink)	1.8
8	50 % calcined rock, 8.5 % NaOH, 41.5 % Ural clay (yellow)	1.9
9	50 % calcined rock, 8.5 % NaOH, 41.5 % Astana clay (white)	2.7
10	50 % calcined rock, 8.5 % NaOH, 41.5 % Uzbek clay (blue)	4.2
11	50 % calcined rock, 8.5 % NaOH, 41.5 % dried activated sludge	7.6
12	50 % calcined rock, 8.5 % NaOH, 41.5 % red clay	11.74
13	50 % calcined rock, 8.5 % NaOH, 41.5 % Aktobe clay (white)	18.6
14	50 % dried activated sludge, 8.5 % NaOH 41.5 % Fe_2O_3	25
15	50 % calcined rock, 8.5 % NaOH, 41.5 % ZnO	34.4
16	50 % calcined rock, 8.5 % NaOH, 41.5 % Fe_2O_3	38.9
17	40 % calcined rock, 10 % NaOH, 10 % ZnO, 10 % Fe_2O_3, 10 % CuO, 10 % CaO, 10 % MnO	48.2

The obtained results of sulfur capacity of the developed compositions from natural materials are consistent with the literature data. The sulfur capacity of the obtained adsorbents consists of a set of physical and chemical characteristics. Thus, natural materials (clay, sand, uncalcined rock, iron oxide, zinc oxide) have predominantly a large specific surface due to microporosity. At the same time, calcined sludge, sodium alkali, zinc oxide, iron oxide, manganese, calcium exhibit the ability to chemisorption. Thus, a combined adsorption mechanism is used in the developed materials.

Experiments were conducted with activated sludge to determine its catching capacity in liquid form as an absorbent. Hydrogen sulfide was passed through a suspension with activated sludge, including with the expectation of the biological activity of activated sludge. However, with this method of using this waste, significant results in desulfurization could not be obtained.

In turn, activated sludge, dried after filtration at 100 °C, in the combination of composite materials can show high results in sulfur capacity in comparison with other materials based on minerals.

Under other similar conditions, the best results in terms of sulfur capacity were shown by compositions with red clay and white Aktobe clay.

CONCLUSION

The article presents a literature analysis of adsorbents made from natural materials, and the following materials are selected for use: limestone rock, clays (red, bentonite, kaolin, Uralskaya yellow, Uralskaya blue, Uzbekskaya pink, Astana white, Aktobe white), and activated sludge. Natural materials were preliminarily dehydrated, dried, and calcined and mixed in certain proportions with chemical reagents (sodium hydroxide) for chemical activation. Alkaline earth metal oxides (calcium, zinc, iron) and transition metal oxides (manganese, copper) were added to the composite material to increase its chemisorption capacity.

Seventeen adsorption compositions based on natural materials were proposed, of which seven demonstrated medium and high sorption capacity for hydrogen sulfide. The best properties in terms of sulfur capacity were demonstrated by a composition including 40% calcined rock, 10% NaOH, 10% ZnO, 10 % iron (III) oxide, 10 % CuO, 10 % CaO, 10 % MnO.

All developed adsorption composite materials based on natural minerals have satisfactory physical and chemical characteristics, which together contribute to achieving a high level of absorption capacity in relation to hydrogen sulfide.

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