

Research Results of a Complex Reagent for Wastewater Purification from Hydrogen Sulfide

Kairat Ospanov^{1*}, Erzhan Kuldeyev², Bagdaulet Kenzhaliyev², Elmira Kuldeyeva³

¹ Department of Hydrogeology, Engineering and Oil and Gas Geology, Satbayev University, KR 050013 Almaty, Satbayev Str. 22, Kazakhstan

² Institute of Metallurgy and Ore Beneficiation, Satbayev University KR 050010 Almaty, Shevchenko Str. 29/133, Kazakhstan

³ Satbayev University, KR 050013 Almaty, Satbayev Str. 22, Kazakhstan

* Corresponding author's e-mail: ospanovkairat@mail.ru

ABSTRACT

This article presents the results of research intended to obtain a complex alumina-iron reagent based on natural diatomite and industrial products of alumina production for wastewater purification from hydrogen sulfide. The material composition of the obtained samples using X-ray diffraction analysis was determined. The results of interaction research in the $\text{NaFeO}_2 - \text{H}_2\text{S} - \text{H}_2\text{O}$ system at 25°C are given. The results of research on wastewater purification from hydrogen sulfide in Almaty city with the use of ferric sulfate, ferric chloride, sodium ferrite and a complex reagent containing iron at the content of 5.1 mg/l H_2S in the initial sample of wastewater were presented.

Keywords: diatomite, alumina, industrial products, reagent, wastewater, hydrogen sulfide.

INTRODUCTION

Hydrogen sulfide is a form of reduced sulfur compounds, which are represented by hydrogen sulfide, hydrosulfides and sulfides, depending on the pH of the medium. At $\text{pH} < 10$ the maintenance of sulfide ions can be neglected, at $\text{pH} = 7$ the maintenance of H_2S and HS^- is approximately equal, at $\text{pH} = 4$ hydrogen sulfide is almost completely (99.8%) in the form of H_2S [Baawain et al. 2018]. Restriction of the concentration of reduced sulfur compounds in waste water directed on biological purification under aerobic conditions is connected not only with their toxic effect on microorganisms [Augusto et al. 2019] but also with the fact that reduced sulfur compounds are energy donors for aerobic bacteria of Thiobacillus genus. Most Thiobacillus can oxidize various sulfur compounds, forming sulfate as the end product. Filamentous sulfur bacteria also actively develop in a medium in which hydrogen sulfide is found. Thus, in the presence of reduced sulfur compounds in biological treatment facilities domestic wastewater develops

the microorganisms that are competitive in the absorption of dissolved oxygen, which violates the balanced process of purification, in particular, the nitrification process can stop and there will be a deterioration in the quality of treated wastewater in general. At present, it is increasingly possible to observe higher concentrations of hydrogen sulfide in wastewater entering the wastewater purification facilities from a settlement. As a rule, this is due to the high duration of wastewater stay in the collectors, as well as the flow to purification facilities of wastewater from cesspools, which are present in the areas that are not canalized [Zwain et al. 2019]. Nowadays, the methods of hydrogen sulfide purification with the use of chemical reagents are more and more popular. One of accessible and effective reagents for oxidation and neutralization of hydrogen sulfide are the compounds of iron in the active form [Majeda et al. 2004]. Reaching maximum values of interaction speed of two- and three-valent iron salts with sulfides of various forms (S^{2-} , HS^- , H_2S) requires regulation of liquid environment at pH values 7–8.

In the work [Mohammad Irani et al. 2011], the results of studies on synthesis of new reagent, representing nanosized iron of zero valence, modified by ethylene glycol and aluminum hydroxide were presented. Such a combination of components allows to increasing the efficiency of the process of removal of sulfides dissolved in water. The use of this complex coagulant makes it possible to remove sulfides from the solution due to the formation of surface complexes, iron mercaptooxide (FeOSH) and a mixture of iron sulfides: FeS, FeS₂, FeS_n. The hydrogen sulfide solution was oxidized to elemental sulfur by stabilized iron (III) hydroxide deposited on zeolite granules [Wilson 2013]. It was found that zeolite coated with iron hydroxide provides an effective method of hydrogen sulfide removal for relatively small water systems, and its use for purification of drains is unlikely. In [Brigada 2015] the results of studies on regeneration and recycling of granulated iron hydroxide used to remove dissolved hydrogen sulfide from model systems were presented. After oxidation of dissolved hydrogen sulfide to elemental sulfur with simultaneous reduction of solid Fe (III) to Fe (II), the used reagent is regenerated by air oxygen to iron (III) hydroxides.

The reagent prepared from a mixture of granulated hydroxide of trivalent iron, granulated iron oxide and spent iron crusts is able to remove hydrogen sulfide from deposits and water in drains and can be regenerated when in contact with dissolved oxygen [Kofman 2012]. The authors of the research [Churikova et al. 2016] studied the possibility of using crude and modified diatomite for additional purification of secondary wastewater. For the purification of drinking water and wastewater from a number of harmful substances, including hydrogen sulfide, the Fernel reagent (Russia) based on sodium ferrate Na₄FeO₅, which turns into trivalent iron hydroxide during reduction, is currently proposed [Orekhova et al. 2014]. Thus, iron compounds are estimated as one of the most effective in hydrogen sulfide purification. Speed and completeness of process of adsorption of the dissolved hydrogen sulfide by iron compounds is largely determined by a form of iron hydroxides in water solutions. The colloidal compounds have greatest reactivity, which can be obtained by hydrolysis from various acidic iron compounds (nitrates, chlorides, sulfates). At the same time, the search for more economical methods of obtaining active forms of iron hydroxides remains relevant. The purpose of the research is to develop the technology of obtaining a complex

aluminous iron reagent based on natural diatomite, sodium aluminate-ferrite and industrial products of alumina production for wastewater purification from hydrogen sulfide.

MATERIALS AND METHODS

In 2020, the authors developed a technology to obtain a complex aluminous iron reagent based on sodium ferrite, ferruginous diatomite and iron compounds. Reagent natural material was used to obtain the reagent – ferruginous diatomite of the Zhalpak deposit in the Aktobe region, synthesized sodium ferrite and ferruginous sands from industrial waste of the aluminum plant in the Pavlodar city of the Republic of Kazakhstan. The initial material was crushed finely in order to obtain a pilot batch of ferruginous diatomite. According to the results of the X-ray phase analysis, the iron-containing minerals in diatomite are: jarosite K(Fe_{0.92}Al_{0.08})₃(SO₄)₂(OH)₆ (10,1%) and goethite Fe⁺³O(OH) (6.9%), the silicon-containing minerals are quartz (53.6%), microcline, albite, megacalsilite, illite and aluminosilicate sodium (Table 1). Sodium ferrite was produced by sintering trivalent iron oxide with soda according to the reaction:



For research, a mixture from the components crushed in a porcelain mortar were prepared beforehand, containing their equivalent quantities. The initial charge was pressed on a Metallkraft WWP 50 M press with a specific pressure of 30 mPa (300 kgf/cm²) to provide maximum particle contact. Pellets with a diameter of 17 mm, a height of 17–20 mm were obtained on a metal platform punch and matrix. The sintering process was performed in a muffle furnace at temperatures of 800 and 900°C during 1 and 2 h.

The material composition of the obtained samples was determined using X-ray diffraction, X-ray fluorescence and chemical analysis. From the data of X-ray diffraction analysis, it follows that at a temperature of 800°C the reaction of sodium ferrite synthesis does not occur, since the composition of the initial mixture of reagents does not change. A product containing 100% sodium ferrite was obtained under optimal conditions of synthesis – temperature 900°C and sintering process duration 1 h – (Fig. 1). Iron sands are a waste of alumina production with a high content of iron oxide – 50.12% (Table 2). X-ray phase analysis of the

Table 1. Phase composition of diatomite according to X-ray phase analysis

No.	Compound name	Formula	Content, %
1	Quartz	SiO ₂	53.6
2	Jarosite	K(Fe _{0.92} Al _{0.08/3})(SO ₄) ₂ (OH) ₆	10.1
3	Microcline	KAlSi ₃ O ₈	7.0
4	Albite	NaAlSi ₃ O ₈	6.9
5	Goethite	Fe ⁺³ O(OH)	6.9
6	Megacalcite	K(AlSiO ₄)	5.7
7	Illite	(K,H ₃ O)Al ₂ (Si ₃ Al)O ₁₀ (OH) ₂ ·xH ₂ O	5.1
8	Sodium aluminosilicate	Na _{1.15} Al _{1.15} Si _{0.85} O ₄	4.7

sample of iron sands showed the presence of iron compounds in the form of hematite – trivalent iron oxide, magnetite – oxides of two – and trivalent iron, srebrodolskite, the content of which in the sample in total is 55.62% (Figure 2). The following phases were also found in the sample: sodium-aluminum silicate, calcium, silicon, aluminum oxides, perovskite, and cristobalite. Thus, a batch of iron-containing reagent, including sodium ferrite and ferric diatomite, was prepared in the amount of 400g for conducting experiments on wastewater.

RESULTS AND DISCUSSION

Results of interaction in the NaFeO₂ – H₂S – H₂O system at 25°C

The system NaFeO₂ – H₂S – H₂O at 25°C was studied to simulate the interaction of hydrogen sulfide with iron compounds in the active form. Standard sample was used to prepare a hydrogen sulfide solution of a given concentration. The standard sample is an aqueous sodium sulfide solution of 5

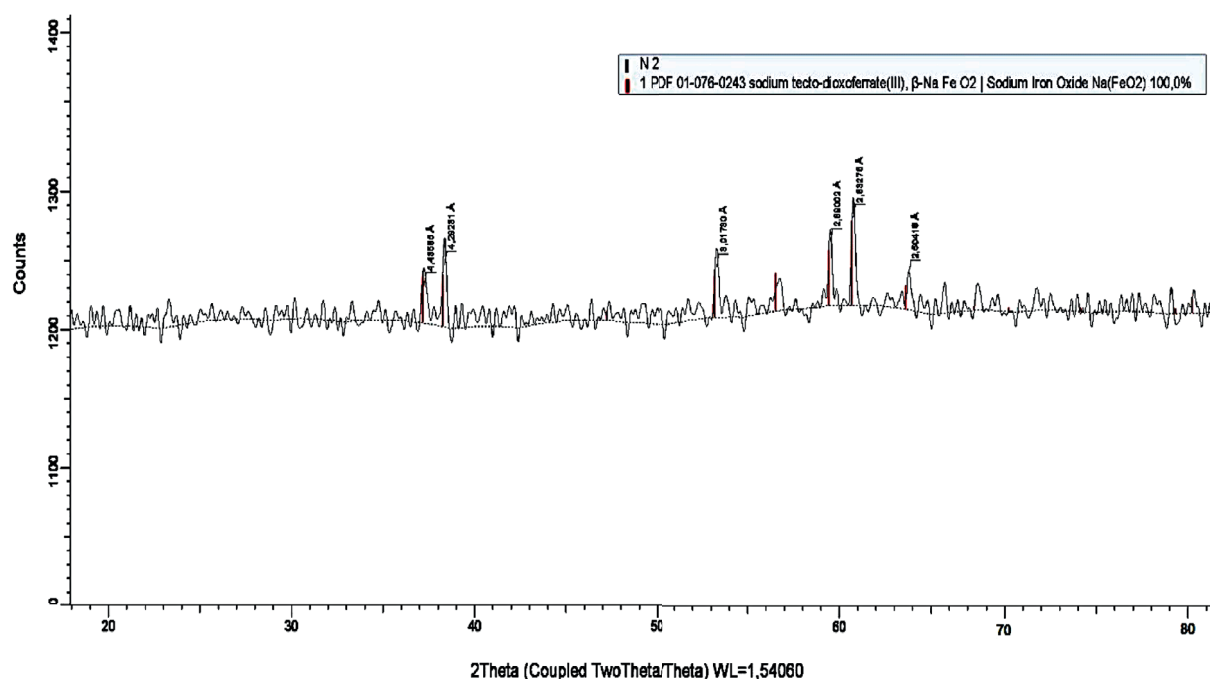


Figure 1. X-ray of the sintering product of the charge Fe₂O₃ + Na₂CO₃ at 900°C

Table 2. Results of chemical analysis of iron sands of “Pavlodar Aluminum Plant” JSC

Name of the samples	Chemical content, mass %								
	Na ₂ O	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	CaO	SO ₃ ²⁻ general	K ₂ O	TiO ₂	Cl ⁻
Iron sands	0.63	15.43	5.68	50.12	5.38	1.42	0.112	2.2	0.018

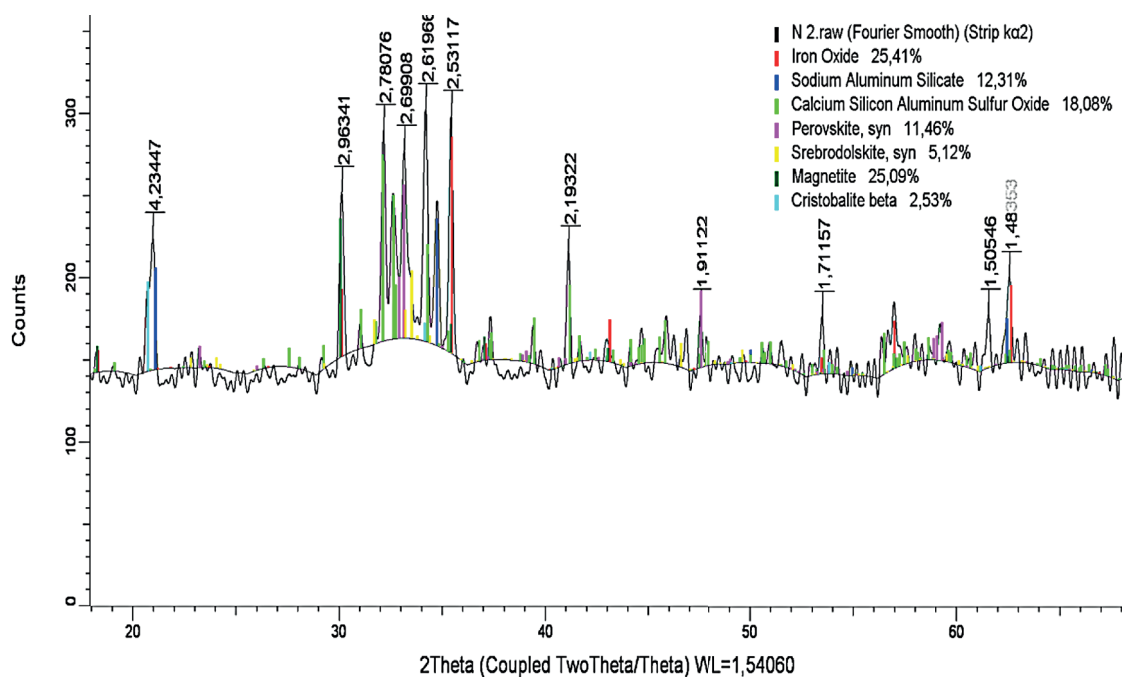


Figure 2. X-ray of the sample of iron sands

cm³ with a mass concentration of sulfide ions of 1 g/dm³. Ampoules were opened at room temperature, the contents were poured into an appropriate measuring flask with a friction cap, and the solution in the flask was filled to the mark with distilled water. The required volume of the standard sample was preliminarily calculated by the formula:

$$V_{CO} = 0.001 C_X V_K / C_m \quad (2)$$

where: C_X – the value of the mass concentration of sulfide ions in the prepared solution, mg/dm³;

C_m – the certified value of the mass concentration of sulfide-ions in the sample, g/dm³;

V_K – volume of the used measuring flask, cm³.

The essence of the reagent methods intended to remove hydrogen sulfide dissolved in water is to add chemical reagents to the processed water, reacting with H₂S, which results in its oxidation to sulfates or transfer it into less active compounds, including sulfides. Hydrogen sulfide in wastewater is in the form of an undissociated compound (H₂S), hydrosulfide ions (HS⁻) and sulfide ions (S²⁻). The ratio between these forms is determined by the pH of the water, much less affected by temperature and mineralization.

At pH < 7, the main form of hydrogen sulfide existence in water is H₂S, at pH > 7 in solution HS⁻ dominates, the presence of S²⁻ ion is possible

only at pH > 10. Photocolorimetric, according to ST RK 2874-2016 [ST RK 2874-2016, 2016] and titrimetric, according to GOST 26449.3-85 [GOST 26449.3-85. 2003] analysis methods were used for determination of the hydrogen sulfide content in the studied systems. The photometric method for determining the mass concentration of hydrogen sulfide and sulfides is based on their ability in acid medium to form N,N-dimethyln-phenylenediamine with oxidation products in the presence of iron salts (Sh) methylene blue, intensity of coloring which is proportional to the content of hydrogen sulfide and sulfides. The titrimetric method of analysis is to precipitate sulfide ions as cadmium sulfide and oxidize them with iodine. Excess iodine is titrated with sodium sulfate solution (Na₂S₂O₃·5H₂O) to a light-yellow color, starch is added and titrated until discoloration.

Mass concentration of hydrogen sulfide X, mg/dm³, was calculated by the formula:

$$X = (V_1 - V_2) \cdot 0.852 \cdot 1000 / V \quad (3)$$

where: V_1 is the volume of iodine solution added to the test solution, cm³;

V_2 – volume of sodium hydroxide solution used for titration, cm³;

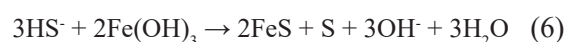
0.852 – mass of hydrogen sulfide, equivalent to the mass of sodium disulfate in 1 cm³ of a solution with a molar concentration of the equivalent of 0.05 mol/dm³, mg; V – volume of the test solution taken for analysis, cm³.

The results of determination of the hydrogen sulfide content in the studied solutions using the photolorimetric method, were not correct enough due to the interfering presence of impurities in the natural material - diatomite and industrial products of alumina production. When the study was conducted to remove hydrogen sulfide in model solutions and wastewater using different precipitant reagents, the control of hydrogen sulfide levels was performed by titrimetric method of analysis. Diatomite; sodium ferrite NaFeO_2 received by synthesis from chemical reagents; sodium ferrite-aluminate $\text{Na}(\text{Fe}_{0.75}\text{Al}_{0.25})\text{O}_2$, received based on iron sands (a waste of alumina production) were tested as reagents for chemical precipitation of hydrogen sulfide. A precipitant in the amount stoichiometric and twofold with hydrogen sulfide was transferred in a volumetric flask containing a model solution with a given concentration of hydrogen sulfide. The content of the flask was thoroughly mixed, then the flask was sealed with a fused cap with paraffin to avoid the loss of H_2S . The results of studies are shown in tables 3 and 4. At 5 and 10 mg/L H_2S in the initial solution, ferrous sulfate and ferric chloride trivalent showed the greatest efficiency. The sodium ferrites synthesized by sintering ferric oxide (III) with soda and those obtained by using iron sands showed practically the same effect as precipitating agents: their introduction into an aqueous solution with dissolved hydrogen sulfide reduced its content by

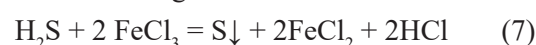
30 and 25, respectively. Diatomite has an insignificant effect on reducing the level of hydrogen sulfide in the solution. Sodium ferrites are hydrolyzed by the reactions:



when they are leached with water. The hydro-sulfide ion present in a slightly alkaline medium and interacts with iron hydroxide to form iron sulfides:



The interaction of H_2S with ferric chloride proceeds according to the reaction:



Reaction of H_2S with iron sulfate:



Results of a research on wastewater purification from hydrogen sulfide in the city of Almaty

The Almaty city wastewater purification facilities are located 12 km to the north-west of the city border, in the Ili district of the Almaty region, south-west of the Zhapek Batyr settlement, on the banks of the Bolshaya Almatinka river. The design (planned) capacity of mechanical and biological purification facilities is 640 thousand m^3 per day. Wastewater sampling

Table 3. Results of hydrogen sulfide determination in the system model solution – reagent (at the H_2S content in the initial solution of 5 mg/l)

No. of sample	Sample Name	H_2S content, mg/l (residual)	H_2S content, % (residual)
1	Initial model solution	5.0	100
2	Initial model solution + diatomite	4.2	84
3	Initial model solution + sodium ferrite NaFeO_2	3.5	70
4	Initial model solution + sodium ferrite-aluminate $\text{Na}(\text{Fe}_{0.75}\text{Al}_{0.25})\text{O}_2$	3.7	74

Table 4. Results of hydrogen sulfide determination in the system model solution - reagent (with H_2S content in the initial solution of 10 mg/l)

No. of sample	Sample Name	H_2S content, mg/l (residual)	H_2S content, % (residual)
1	Initial model solution	10.0	100
2	Initial model solution + $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	1.4	14
3	Initial model solution + $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	1.48	14.8
4	Initial model solution + + sodium ferrite NaFeO_2	7.1	71
5	Initial model solution + sodium ferrite-aluminate $\text{Na}(\text{Fe}_{0.75}\text{Al}_{0.25})\text{O}_2$	7.6	76

for testing of complex iron coagulant was performed on September 29, 2021 at the beginning of purification facilities, that is, in the receiving chamber. Experiments were performed to purify wastewater from hydrogen sulfide using iron salts, sodium ferrite and a complex coagulant including iron diatomite, sodium ferrite and iron salt. The presence of hematite (oxide $\alpha\text{-Fe}_2\text{O}_3$) and goethite (hydroxide $\alpha\text{-FeOOH}$) in the diatomite sample was determined by Mössbauer analysis. Research was performed to determine the specific surface of the diatomite particles using BET analysis (Brunauer, Emmett, Teller method). Four samples were investigated by using the BET method by low-temperature adsorption of nitrogen. Table 5 shows the results for determining the specific surface area, the total pore volume in the gas phase and the pore volume of the diatomite samples in terms of liquid, whereas Figure 3 presents the pore size distribution. On the basis of the data, a sufficiently large surface of the interaction of iron hydroxides in the composition

of diatomite with hydrogen sulfide ions can be confirmed. The use of diatomite as a highly porous material contributes to chemisorption and the reaction of interaction of iron compounds in the complex coagulant with hydrogen sulfide. Iron salts, sodium ferrite NaFeO_2 obtained by synthesis from chemical reagents and a complex iron-containing reagent including diatomite, sodium ferrite and iron sulfate (as a pH regulator) were tested as reagents to remove hydrogen sulfide from wastewater. All samples were left for an additional 6 hours; after that they were used as reagents for the removal of hydrogen sulfide from wastewater (Figure 4).

The efficiency of sulfide removal for iron sulfate was 76.43%, iron chloride was 74.51%, sodium ferrite was 23.5%, and the complex iron-containing coagulant was 73.53% at the H_2S content of 5.1 mg/l in the initial wastewater sample. The results are shown in Table 6. Thus, the results of test experiments on removal of hydrogen sulfide from wastewater with the use of a complex iron coagulant showed its sufficient effectiveness.

Table 5. Specific surface area and total pore volume

Sample	SW, m ² /g	V _{ADSMAX} , ml/g	V _{hist.} , ml/g
No. 1	29.41	68.52	0.1068
No. 2	29.96	67.30	0.1049
No. 3	42.70	71.68	0.1117
No. 4	41.99	66.82	0.1041

Note: SW – specific surface area, m²/g; V_{ADSMAX} – total pore volume at gas filling, ml/g; V_{hist.} – total true pore volume (in terms of the liquid phase), ml/g.

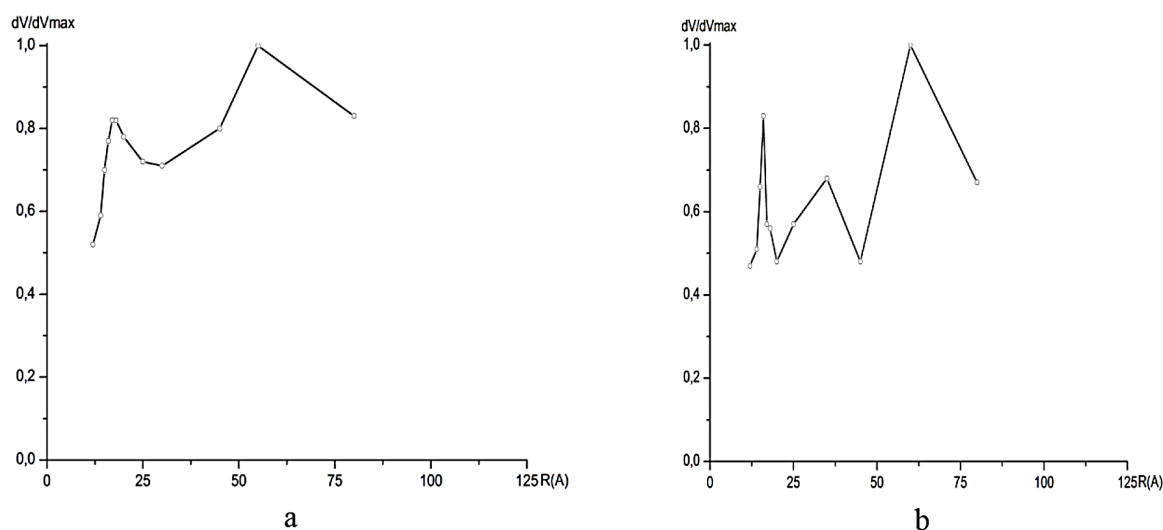


Figure 3. Distribution of pores by size; a) sample 1; b) sample 2; c) sample 3; d) sample 4 (R(A) – pore radius in angstroms; dV/dVmax – ratio of pore volume of given radius to maximum volume)

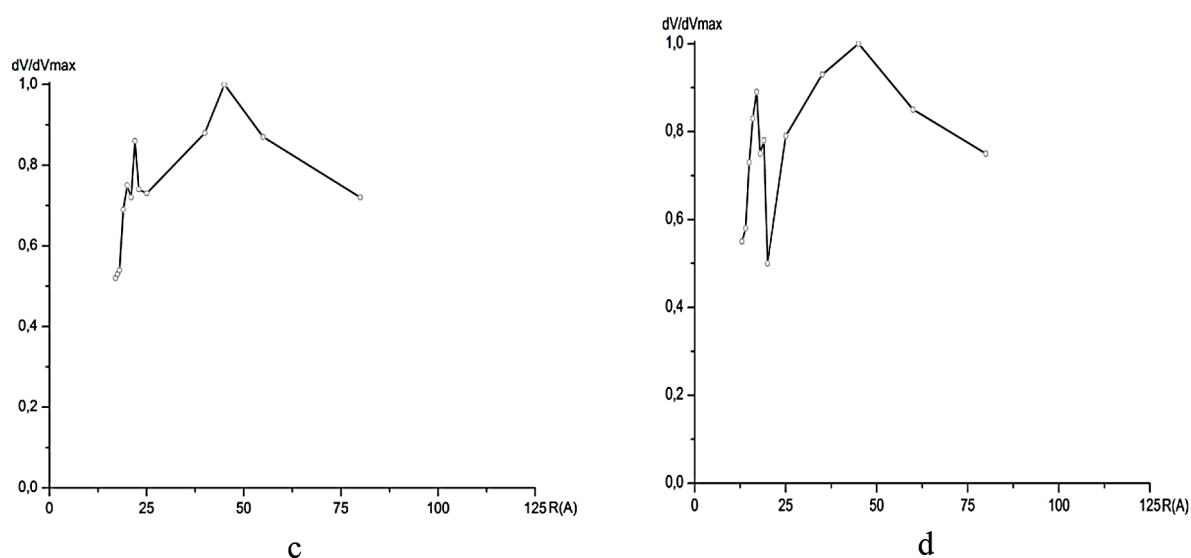


Figure 3c & 3d. Cont. Distribution of pores by size; a) sample 1; b) sample 2; c) sample 3; d) sample 4 (R(A) – pore radius in angstroms; dV/dVmax – ratio of pore volume of given radius to maximum volume)



Figure 4. Samples for laboratory tests

Table 6. Results of hydrogen sulfide determination in wastewater system – reagent (at the H₂S content in wastewater equal to 5.1 mg/l)

No. of sample	Sample Name	H ₂ S content, mg/l (residual)	H ₂ S content, % (residual) H ₂ S
1	Wastewater	5.1	100
2	Wastewater + FeSO ₄ · 7H ₂ O	1.2	23.53
3	Wastewater + FeCl ₃ · 6H ₂ O	1.3	25.49
4	Wastewater + NaFeO ₂	3.9	76.5
5	Wastewater + (diatomite + NaFeO ₂ + FeSO ₄ · 7H ₂ O)	1.35	26.47

CONCLUSIONS

The technology intended to obtain a complex aluminum-iron reagent based on natural diatomite and industrial products of alumina production was developed. Natural material, i.e.

– ferruginous diatomite of the Zhalspak deposit in the Aktobe region and synthesized sodium ferrite from industrial waste of the aluminum plant in the Pavlodar city of the Republic of Kazakhstan was used to obtain the reagent. Initial material was crushed finely in order to obtain a pilot batch of

ferruginous diatomite. The obtained material in the form of a finely ground powder was used for purification of wastewater from hydrogen sulfide. A batch of the complex iron-containing reagent, including sodium ferrite sodium ferrite and iron diatomite in the quantity for carrying out test experiments on the wastewater. The X-ray phase analysis of a sample of the synthesized product revealed the presence of one NaFeO_2 phase.

The interaction in $\text{NaFeO}_2 - \text{H}_2\text{S} - \text{H}_2\text{O}$ system was studied. At the content of 5 and 10 mg/l H_2S in the initial solution, divalent iron sulfate and trivalent iron chloride showed the highest efficiency. Diatomite has an insignificant effect on reducing the level of hydrogen sulfide in the solution. The experiments were performed to purify wastewater from hydrogen sulfide using iron salts, sodium ferrite and a complex reagent including ferrous diatomite, sodium ferrite and iron salt. The efficiency of sulfide removal for iron sulfate was 76.43%, for iron chloride – 74.51%, for sodium ferrite – 23.5%, for complex iron-containing reagent – 73.53% at the H_2S content of 5.1 mg/l in the initial sample of waste water.

Thus, the results of test experiments on removal of hydrogen sulfide from wastewater with the use of a complex iron coagulant showed its sufficient effectiveness.

Acknowledgements

We appreciate the support of the Ministry of Education and Science of the Republic of Kazakhstan. This work was performed with financial support from the Committee on Science of the Ministry of Education and Science of the Republic of Kazakhstan [Grant AP08855852 “Development of technology for obtaining a complex coagulant based on iron diatomite for purification of industrial and waste water from hydrogen sulfide”]

REFERENCES

1. Augusto M.R., Campos B., Carvalho V.S.B., Calheiros H.C. 2019. Modeling of H_2S dispersion in Brazil with Aermol: Case study of water resource recovery facility in south of Brazil. *Rev. Bras. Meteorol.*, 34, 497–504.
2. Baawain M., Al-Mamun A., Omidvarborna H., Al-Sulaimi I.N. 2018. Measurement, control, and

modeling of H_2S emissions from a sewage treatment plant. *Int. J. Environ. Sci. Technol.*, 16, 2721–2732.

3. Brigada Y.V. 2015. Hydrogen sulfide as a factor of environmental hazards of gaseous emissions from drainage networks. *Bulletin of the Kharkiv National Automobile and Road University*, 69, 101–104. http://nbuv.gov.ua/UJRN/vhad_2015_69_19
4. Churikova L.A., Uarisov D.D. 2016. Review of methods to control sulfur dioxide during oil production. *Technical Sciences: Problems and Prospects: Proceedings of the IV International Scientific Conference*. St. Petersburg, 67–73. https://moluch.ru/conf/tech/archive/166/10_954/
5. GOST 26449.3-85. 2003. Stationary distillation desalting units. Methods of saline water and distillate chemical analysis on gas content. USSR National Committee on Standards. PPC Publishing House of Standards.
6. Kofman V.Y. 2012. Hydrogen sulfide and methane in drainage networks (review). *Water Supply and Sanitary Engineering*, 11, 72–78. <http://www.vstmag.ru/ru/archives-all/2012/2012-11/3291-serovodorod-i-metan>
7. Khraisheh M.A.M., Al-degs Y.S., Mcminn W.A.M. 2004. Remediation of wastewater containing heavy metals using raw and modified diatomite. *Chemical Engineering Journal*, 99(2), 177–184.
8. Irani A., Amjadi M., Mousavian M.A. 2011. Comparative study of lead sorption onto natural perlite, dolomite and diatomite. *Chemical Engineering Journal*, 178, 317–323.
9. Orekhova A.I., Halemsky A.M., Sherstobitova T.M., Kogan B.S., Ivanov A.V. 2014. Reagent - oxidant of the brand “Fernel” for decontamination and purification of aqueous solutions. *Chemistry and chemical technology.*, 57(3), 128–131.
10. ST RK 2874-2016. Water quality. Photometric method for the determination of hydrogen sulfide and sulfides. Approved and put into effect by Order of the Chairman of the Committee for Technical Regulation and Metrology of the Ministry for Investment and Development of the Republic of Kazakhstan No. 299-od dated 24.11.2016.
11. Wilson Y.V. 2013. Studies in the removal of reduced sulfur compounds from wastewater. *Internet Journal Naukovedenie*, 3, 1–10. <https://cyberleninka.ru/article/n/issledovaniya-v-oblasti-udaleniya-vosstanovlennyh-soedineniy-sery-iz-stochnyh-vod/viewer>
12. Zwain H.M., Vakili M., Faris A.M., Dahlan I. 2019. Modeling the fate of phenol in moving bed biofilm reactor sewage treatment plant. In: *Proc. AICCE’19. AICCE 2019. Lecture Notes in Civil Engineering* (ed. Mohamed-Nazri F.). Springer, Cham.