WATER PURIFICATION FROM HYDROGEN SULPHIDE USING CLINOPTYLOLITE MODIFIED WITH MANGANESE OXIDES

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Hydrogen sulphide is contained in many types of groundwater and mine waters. These waters can serve as an additional resource for drinking water, but their thorough purification from hydrogen sulphide is necessary, since the regulatory documents in force in Ukraine do not allow the presence of H_2S *in drinking water. The most effective methods of water purification from* H_2S *are oxidative-catalytic, in particular, using manganese oxides (*Mn_xOy*) deposited on a carrier as a catalyst. The authors developed a new method for modifying sorbents with* Mn_xO_y *particles by impregnating natural clinoptilolite with* $Mn(NO_3)_2$ *solutions with its subsequent decomposition under the influence of microwave electromagnetic radiation. The resulting sorbent, modified with* Mn_xO_y *particles, was used in studies of hydrogen sulphide oxidation in model solutions with a concentration of 10 mg/L. The studies were conducted under anaerobic conditions and in the presence of oxygen, which provided air bubbling at a flow rate of 50 to 300* cm^3*/min through a layer of modified clinoptilolite, which was located in a glass column. The pH value of the model solution (6.0; 7.0 and 8.5) and temperature (15, 20, 25 and 30 ºC) were also variable parameters. It was found that the value of the rate constant increased not only with increasing temperature and air flow rate, but also with increasing pH of the medium. An increase in pH of the medium causes a decrease in the redox potential of the oxidant, but at the same time contributes to a shift in the equilibrium in the* $H_2S–HS^-$ *system towards the ionic form of hydrogen sulphide. This provides a higher rate of its oxidation. The calculated values of the Van't Hoff temperature coefficient (2.0…3.7) and the activation energy of* H_2S *oxidation (53…67 kJ/mol) indicate that the process proceeds in the kinetic region. It was established that at pH from 7.0 and above and at an air flow rate of about 200* cm^3*/min (under experimental conditions), the degree of hydrogen sulphide oxidation within 60 min approaches 100%. Thus, the conducted studies confirmed the high efficiency of the obtained sorbent modified with* Mn_xO_y *particles.*

Keywords: *clinoptilolite, hydrogen sulphide, manganese oxides, modification, sorbent, water purification*

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1. Introduction

An acute problem in Ukraine today is the reduction of natural water supplies suitable for human consumption. The problem is exacerbated by the pollution of drinking water sources caused by russian aggression. Therefore, the search for alternative sources of water supply and the involvement of waters whose quality does not meet the requirements of regulatory documents in the field of water use is becoming increasingly relevant. For example, these include groundwater containing hydrogen sulphide. Typically, the hydrogen sulphide content in groundwater is within 0.5…1.0 mg/L. However, the smell of hydrogen sulphide is clearly felt at its content of 0.3 mg/L (odor threshold ~0.0005 mg/L), which affects the organoleptic characteristics of water. Mine waters are also considered as a potential drinking water resource (Shvets at al., 2025, Clay at al., 2022), which, together with hydrogen sulphide (0.5…20 mg/L), contain many organic compounds and compounds of many metals (Bosak at al., 2020). In addition, sulphide sulphur compounds (hydrogen sulphide, hydrogen sulphide ions, sulphide ions) are contained in wastewater from oil refining and coke chemical (5…100 mg/L), pulp and paper (up to 20 mg/L), food (up to 10 mg/L) industries, etc. (Bosak at al., 2020, Ministry of Environmental, 2023). In addition, given the difficult situation with the state of water supply sources in combat zones and territories damaged by military actions, groundwater can be another resource of drinking water, at least temporarily. Due to the prevalence of reducing conditions in soils, sulphide sulphur compounds, hydrogen sulphide in particular, are often also found in groundwater.

Hydrogen sulphide is a cellular poison because it blocks enzymes (in particular, cytochrome-c-oxidase), practically stops tissue respiration and causes hypoxia. The presence of hydrogen sulphide in its undissociated (molecular) form causes its toxicity, since it easily penetrates the tissues of the body.

Given the low odor threshold and potential toxicity, according to DSanPiN 2.2.4-171-10, the presence of hydrogen sulphide in drinking water is not allowed.

Physical and chemical methods are used to remove hydrogen sulphide from water. Physical methods consist in the desorption of hydrogen sulphide by blowing water with air. At the same time, part of the hydrogen sulphide is oxidized to dispersed sulphur, less to sulphates. The speed of such processes is low and significantly depends on the composition of the water.

A significantly higher rate of hydrogen sulphide oxidation is achieved when catalytic-oxidative systems are used. These systems are much less sensitive to the salt composition of water and the form of hydrogen sulphide in water (molecular (H_2S) or ionic (HS^-)). Manganese oxides (MnO_2, Mn_2O_3, Mn_3O_4) are used as heterogeneous catalysts (Maroño at al., 2021; Avetisyan at al., 2021), iron compounds (Fe_2O_3, iron(III) hydroxide or oxyhydroxide) (Sun at al. 2014), copper oxides (CuO, Cu_2O), cobalt (Co_3O_4), nickel (NiO), cerium (CeO_2) (Palma at al., 2013). Liquid-phase catalytic systems include Fenton and Fenton-like systems, biocatalytic systems based on thiobacteria (e.g., *Thiobacillus, Acidithiobacillus*). Very high oxidative capacity is inherent in photocatalytic systems based on TiO_2, Fe_2O_3, ZnO, CdS, C_3N_4. Under the influence of ultraviolet or visible light, electrons are generated in the catalysts, which oxidize hydrogen sulphide to sulphur or sulphate ion (Yan at al., 2023; Yang at al., 2023; Zhou at al., 2023). However, the efficiency of the process significantly depends on the optical transparency of the water. Dispersed particles in water significantly limit the penetration of light into the water column.

In recent years, research on the electrochemical oxidation of hydrogen sulphide in aqueous environments has been developing (Sergienko at al., 2023; Velazquez-Rizo at al., 2023).

At the same time, together with dissolved pollutant compounds, hydrogen sulphide in particular, the above waters contain dispersed particles of various nature. They also significantly deteriorate water quality. Therefore, they also need to be removed from the waters. It is obvious that the processes of purifying waters containing hydrogen sulphide and heterophase particles of varying degrees of dispersion are usually multi-stage. One of the main factors when choosing water purification methods to obtain drinking-quality water is economic feasibility (Dvořáček et al., 2022). Therefore, it is advisable to use such purification methods that combine several technological stages, in particular, filtration, sorption and oxidation of compounds with reducing properties, in particular, hydrogen sulphide.

For this purpose, filter media are used, on which catalytically active compounds are applied, for example, metal oxides mentioned above. High efficiency is characteristic of catalytic systems formed on activated carbon, clays, synthetic or natural zeolites.

One of the most common catalysts immobilized on various carriers is manganese(IV) oxide. It is characterized by a high redox potential (+1.23 V). Usually MnO_2 is applied to quartz sand, ceramics (Shrestha et al., 2024), zeolites (Jin, 2023). As a rule, manganese(IV) oxide is synthesized by the interaction of manganese chloride and potassium permanganate (Jin et al., 2023). However, synthetic carriers are expensive, and potassium permanganate is a precursor whose use is limited.

The aim of the work was to study the process of catalytic oxidation of hydrogen sulphide in model solutions using clinoptilolite modified with manganese oxides according to the method developed by the authors.

2. Materials and Methods

The studies used natural clinoptilolite from the Sokyrnytsa (Ukraine) deposit with a dispersion of 1.0…1.5 mm, which was pre-enriched according to the method (Pyrih, 2024). The enriched clinoptilolite was modified with a manganese nitrate solution under mechanical stirring (Pyrih & Znak, 2025). After modification, the clinoptilolite was placed in a “Samsung” microwave oven (power 500 W, radiation frequency 2.45 GHz), where under the action of electromagnetic radiation, manganese nitrate decomposes with the formation of manganese(IV) oxide according to the reaction

$$Mn(NO_3)_2 \rightarrow MnO_2 + 2NO_2.$$

In partly decomposition occurred with the formation of Mn_2O_3 according to the equation

$$4Mn(NO_3)_2 \rightarrow 2Mn_2O_3 + 8NO + 5O_2.$$

The obtained modified sorbent was used as a filter loading for the oxidation of hydrogen sulphide in model solutions. Model solutions were obtained by saturating distilled water with hydrogen sulphide, which was generated during the interaction of Na_2S and H_2SO_4 solutions (25%) until a concentration of 10±0.1 mg/L was reached. To create a model solution with a given pH value ((6.0; 7.0; 8.5)±0.1), solutions (0.01 mol/L) of hydrochloric acid or sodium hydrogen carbonate with. The integral concentration of hydrogen sulphide (H_2S and HS^-) in aqueous model solutions was determined potentiometrically using a sulphide-selective electrode ESS-01 according to the developed method.

The study was carried out using the installation (Fig. 1). Modified clinoptilolite was loaded into a glass column equipped with nozzles for water sampling to determine the hydrogen sulphide content. This made it possible to determine the concentration of H_2S depending on the residence time in the column, that is, depending on the duration of oxidation.

The study was conducted at a temperature of 15…30 ºC. For this purpose, the solution that entered the column 3 from the vessel 1 through the rotameter 2, and the air that was supplied by the compressor 4 through the rotameter 5, were previously passed through a water thermostat (not shown in Fig. 1), where they were heated to a given temperature.

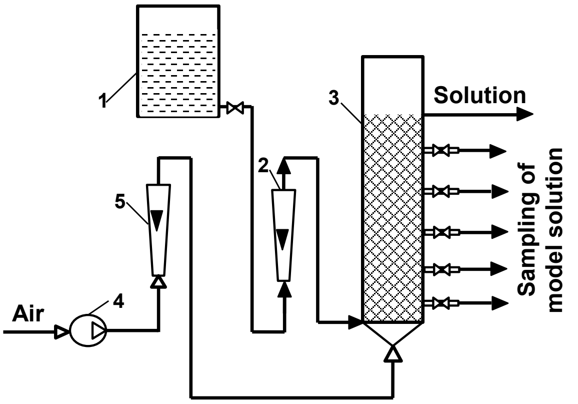

Fig. 1. *Schematic diagram of a laboratory setup for studying hydrogen sulphide oxidation: 1 – tank with model solution; 2, 5 – rotameters, 3 – column with modified clinoptilolite, 4 – air compressor*

For the oxidation of hydrogen sulphide with the participation of a catalyst, air was supplied to the lower part of the column at a consumption of 50…300 mL/min. In a parallel experiment, nitrogen was supplied instead of air to create an oxygen-free environment (pre-prepared model solutions were not deaerated).

3. Results and discussion

In the absence of oxygen in the system (in the case of nitrogen being supplied to column 3), a decrease in the concentration of hydrogen sulphide was initially observed due to its oxidation of manganese oxides immobilized on the surface of clinoptilolite particles. But under anaerobic conditions, regeneration of the catalyst, of course, did not occur. Therefore, the further change in the concentration of H_2S in the solution became smaller and smaller until its oxidation ceased (Fig. 2, curve 1). In the case of creating aerobic conditions in the environment, the change in the concentration of H2S occurred much more intensively (Fig. 2, curves 2–5), which indicated a significant increase in the oxidation rate.

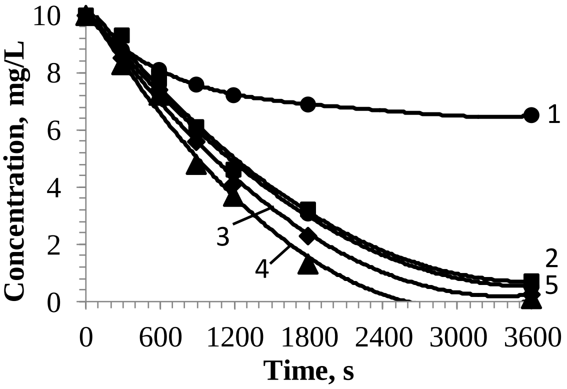

Fig. 2. *Dependence of H_2S concentration on time in anaerobic (1) and aerobic conditions (pH 7.0; 20ºC);*
air consumption (cm^3/min): 2 – 50; 3 – 100; 4 – 200; 5 – 300.

When the air consumption increased from 50 to 200 cm^3/min, the oxidation rate naturally increased due to the increase in the contact area in the three-phase system (air – clinoptilolite – solution) and the increase in the concentration of dissolved oxygen in the solution. However, with a further increase in the air flow rate to 300 cm^3/min, the oxidation rate decreased. This was probably due to the blocking of clinoptilolite particles by air bubbles and, as a result, a decrease in the contact area of the phases. This assumption was confirmed by visual observations.

The corresponding values of the rate constant of H_2S oxidation are given in Table 1. Further studies were carried out at air consumption of 50…200 cm^3/min and in a nitrogen environment.

Reducing the process temperature (at pH 7.0) to 15 ºC naturally caused a slowdown in H_2S oxidation Fig. 3.

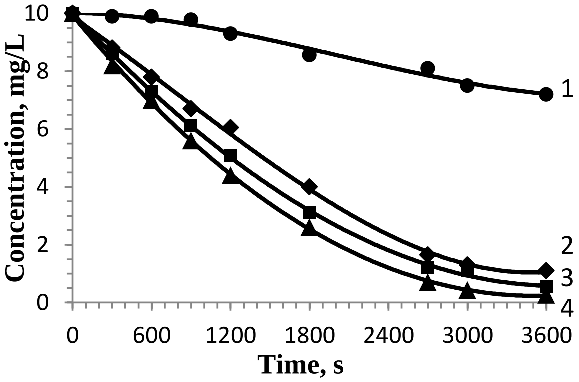

Fig. 3. *Dependence of H_2S concentration on time in anaerobic (1) and aerobic conditions (pH 7.0; 15ºC);*
air consumption (cm^3/min): 2 – 50; 3 – 100;
4 – 200; 5 – 300.

Accordingly, increasing the temperature to 25 and 30 °C (pH 7.0) caused a faster change in the hydrogen sulphide concentration (Fig. 4 and 5).

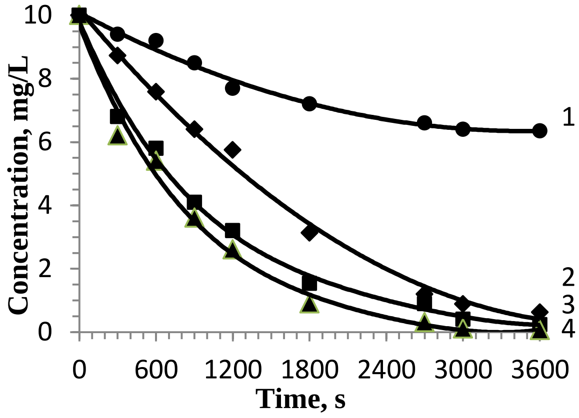

***Fig. 4**. Dependence of H_2S concentration on time in anaerobic (1) and aerobic conditions (pH 7.0; 25ºC);*
air consumption (cm^3/min): 2 – 50; 3 – 100;
4 – 200.

In all cases (at pH 7.0) increasing the air consumption from 50 to 200 cm^3/min leads to more and more complete oxidation of hydrogen sulphide. In contrast to aerobic conditions, in anaerobic conditions the nature of the change in hydrogen sulphide concentration at different temperatures is somewhat different. This is probably due to the heterogeneity of the modified clinoptilolite particles and the different initial oxygen content in the model solutions, which was absorbed from the air during the preparation of the model solutions. The oxidation of hydrogen sulphide in anaerobic conditions occurs only due to the oxidizing ability of manganese oxide

$$MnO_2 + 2H_2S = Mn^{2+} + 2S + 2H_2O.$$

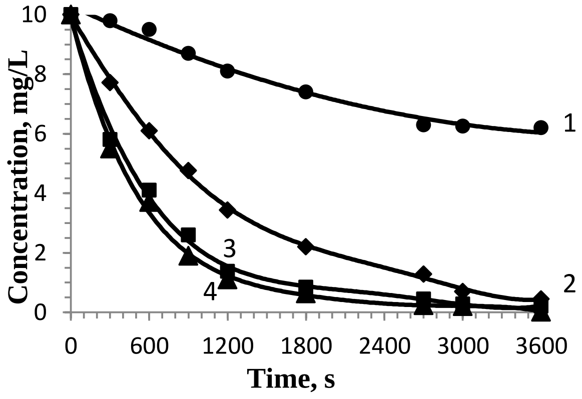

Fig. 5. *Dependence of H_2S concentration on time in anaerobic (1) and aerobic conditions (pH 7.0; 30ºC);*
air consumption (cm^3/min): 2 – 50; 3 – 100;
4 – 200.

The values of the rate constant of H_2S oxidation (total) in model solutions under different conditions are given in Table 1.

As can be seen from Table 1, an increase in temperature naturally causes an increase in the rate constant. However, a clear pattern of the values of the rate constant on temperature (other conditions being the same) was not found. There is also no clear dependence of the values of the Van't Hoff temperature coefficient (γ) on the conditions of the experiments (primarily, temperature).

For example, for different air flows (in the lower temperature range), the value of γ for pH 6.0 varies from 2.2 to 3.7; for pH 7.0 – from 2.4 to 2.9, for pH 8.5 – from 2.5 to 2.9. In the higher temperature range, the value of γ decreases somewhat. The obtained data indicate that the oxidation of hydrogen sulphide as a typical heterogeneous process occurs in the kinetic region. It is obvious that the content of dissolved oxygen and its diffusion in water do not limit the course of the process. The course of the hydrogen sulphide oxidation process in the kinetic region is also evidenced by the activation energy values, which vary for different conditions in the range from 53.1 to 67.5 kJ/mol.

With increasing temperature, the rate of oxygen absorption from the air in the case of a purely physical process decreases. But its partial consumption for the oxidation of hydrogen sulphide (regeneration of the catalyst) causes a shift in the equilibrium, which contributes to its absorption by an aqueous solution.

The lack of a clear dependence of the values of the rate constant and activation energy on temperature may be due to a number of factors: 1) different shapes of clinoptilolite particles; 2) uneven distribution of MnO_2 particles on the surface and near-surface layers of zeolite particles, which is due to the heterogeneity of the surface morphology and chemical composition of zeolite particles; 3) different sizes of MnO_2 particles, which were formed during the decomposition of manganese nitrate at the stage of clinoptilolite modification.

A significant effect of the pH of the medium on the rate of hydrogen sulphide oxidation was found. At lower pH values (pH 6.0), the rate of H2S oxidation decreased (compared to the process at pH 7.0), while at higher pH values (pH 8.5) it increased. This is illustrated by the dependences of H_2S concentration on time for the specified conditions (Fig. 6 and 7) and the value of the H_2S oxidation rate constant (Table 1).

Table 1. *Values of H_2S (total) oxidation rate constants (s^{-1}) depending on temperature, pH and air consumption*

Temperature, °C	**pH**	**Air consumption, cm³/min**		
		50	100	200
15	6.0	$6.05 \cdot 10^{-5}$	$1.024 \cdot 10^{-4}$	$1.71 \cdot 10^{-4}$
	7.0	$2.26 \cdot 10^{-4}$	$5.03 \cdot 10^{-4}$	$6.62 \cdot 10^{-4}$
	8.5	$4.09 \cdot 10^{-4}$	$5.26 \cdot 10^{-4}$	$6.81 \cdot 10^{-4}$
20	6.0	$1.19 \cdot 10^{-4}$	$2.42 \cdot 10^{-4}$	$3.51 \cdot 10^{-4}$
	7.0	$3.90 \cdot 10^{-4}$	$5.42 \cdot 10^{-4}$	$9.21 \cdot 10^{-4}$
	8.5	$5.44 \cdot 10^{-4}$	$8.62 \cdot 10^{-4}$	$9.86 \cdot 10^{-4}$
25	6.0	$0.13 \cdot 10^{-4}$	$3.82 \cdot 10^{-4}$	$4.99 \cdot 10^{-4}$
	7.0	$5.53 \cdot 10^{-4}$	$1.29 \cdot 10^{-3}$	$1.59 \cdot 10^{-3}$
	8.5	$1.13 \cdot 10^{-3}$	$1.33 \cdot 10^{-3}$	$1.70 \cdot 10^{-3}$
30	6.0	$2.42 \cdot 10^{-4}$	$4.26 \cdot 10^{-4}$	$5.42 \cdot 10^{-4}$
	7.0	$8.63 \cdot 10^{-4}$	$1.72 \cdot 10^{-3}$	$1.99 \cdot 10^{-3}$
	8.5	$1.65 \cdot 10^{-3}$	$1.82 \cdot 10^{-3}$	$2.24 \cdot 10^{-3}$

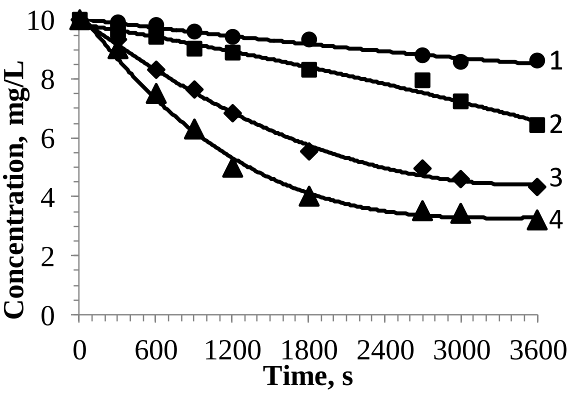

Fig. 6. *Dependence of H_2S concentration on time in anaerobic (1) and aerobic conditions (pH 6.0; 20°C); air consumption (cm^3/min): 2 – 50; 3 – 100; 4 – 200.*

At the same time, the increase in pH in different ranges affects the increase in the rate constant differently. Thus, with an increase in pH from 6.0 to 7.0 at the same temperature, the value of the rate constant generally increases to a greater extent than in the case of an increase in pH from 7.0 to 8.5.

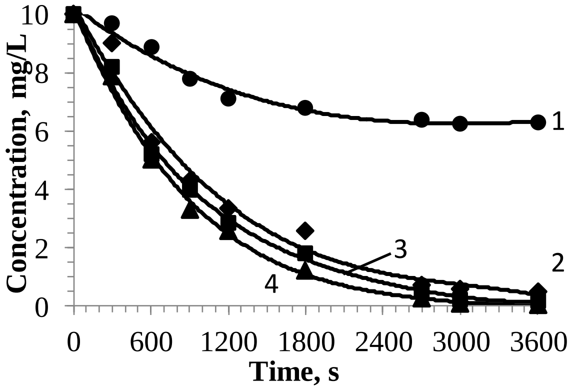

Fig. 7. *Dependence of H_2S concentration on time in anaerobic (1) and aerobic conditions (pH 8.5; 20°C); air consumption (cm^3/min): 2 – 50; 3 – 100; 4 – 200.*

For example, at a temperature of 15 °C and an air flow rate of 50 cm^3/min, with an increase in pH from 6.0 to 7.0, the value of k increases by 3.8 times, and with an increase in pH from 7.0 to 8.5 – by 1.8 times. At 30 °C and a flow rate of 100 cm^3/min, the corresponding increase in the rate constant is 4.1 and 1.1.

At the same time, it is known that with the shift of the pH of the medium to the alkaline region, the value of the RedOx potential decreases, which should negatively affect the rate of H2S oxidation. However, the positive effect of increasing pH on the value of the rate constant is due to the fact that in aqueous solutions hydrogen sulphide is in molecular (H_2S) and ionic (HS^- , S^{2-}) forms. There is an equilibrium between them, which primarily depends on the pH of the solution

$$H_2S \rightleftarrows HS^- + H^+,$$
$$HS^- \rightleftarrows S^{2-} + H^+.$$

Based on the experimentally determined equilibrium constants (pKa_1, pKa_2) for these reactions, the equilibrium content of H_2S and HS^- values at temperatures (15, 20, 25 and 30 °C) and pH (6.0, 7.0 and 8.5) were calculated (Table 2).

Table 2. *Distribution of hydrogen sulphide forms depending on temperature and pH*

Temperature, °C	pH	Contents, %	
		H_2S	HS^-
15	6.0	88.3	11.7
15	7.0	43.1	57.0
15	8.5	7.2	92.8
20	6.0	89.9	10.1
20	7.0	47.1	52.9
20	8.5	8.5	91.5
25	6.0	9.1	90.9
25	7.0	50.0	50.0
25	8.5	1.0	99.0
30	6.0	91.8	8.2
30	7.0	52.9	47.1
30	8.5	4.2	95.8

The content of S^{2-} is not given in the table 2, since its concentration becomes noticeable at pH above 11.5.

At pH 6.0, the molecular form of hydrogen sulphide dominates, due to which the rate of its oxidation is relatively insignificant. Already at pH 7.0, the ratio between the two forms of hydrogen sulphide is practically the same, which causes an increase in the value of the oxidation rate constant. In the weakly alkaline region (pH 8.5), the hydrogen sulphide ion predominates. Therefore, with an increase in pH from 7.0 to 8.5, a significant increase in the rate of the process is observed.

4. Conclusions

Under anaerobic conditions, hydrogen sulphide oxidation occurs only at the initial stages of the process due to the oxidizing ability of manganese oxide. In the presence of manganese oxides in the system, play the role of catalysts for the oxidation of hydrogen sulphide in the liquid phase.

Hydrogen sulphide oxidation in the three-phase system “solid phase (MnO_2) – liquid (H_2S) – gas (O_2)” occurs in the kinetic region; the value of the Van't Hoff temperature coefficient is 2.0…3.7, the activation energy of the heterogeneous oxidation process of H_2S is 53…67 kJ/mol.

Increasing the pH of the aqueous medium from weakly acidic (pH 6.0) to neutral (pH 7.0) or weakly alkaline (pH 8.5) contributes to an increase in the rate of hydrogen sulphide oxidation due to a shift in the equilibrium in the H_2S–HS^- system towards a more reactive ionic form.

The results obtained can be used to develop options for a technological scheme for water purification from hydrogen sulphide, taking into account the pH of the environment. If the water containing hydrogen sulphide is weakly acidic, then its pH must be adjusted to neutral or weakly alkaline before purification from hydrogen sulphide.

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ОЧИЩЕННЯ ВОДИ ВІД СІРКОВОДНЮ З ВИКОРИСТАННЯМ КЛІНОПТИЛОЛІТУ, МОДИФІКОВАНОГО ОКСИДАМИ МАНГАНУ

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Сірководень міститься у багатьох видах підземних та шахтних вод. Ці води можуть слугувати додатковим ресурсом питних вод, однак необхідне їх ретельне очищення від сірководню, оскільки чинними в Україні нормативними документами наявність H_2S *у питній воді не допускається. Найбільш ефективними методами очищення вод від* H_2S *є окисно-каталітичні, зокрема з використанням як каталізатора мангану оксидів (*Mn_xO_y*), нанесених на носій. Авторами розроблено новий метод модифікування сорбентів частинками* Mn_xO_y *шляхом імпрегнування природного клиноптилоліту розчинами* $Mn(NO_3)_2$ *з подальшим його розкладанням під дією надвисокочастотного електромагнітного випромінювання. Отриманий сорбент, модифікований частинками* Mn_xO_y*, було використано у дослідженнях окиснення сірководню у модельних розчинах з концентрацією 10 мг/л. Дослідження проводили в анаеробних умовах та за присутності кисню, що забезпечували барботажем повітря з витратою від 50 до 300* $см^3$*/хв через шар модифікованого клиноптилоліту, який було розташовано у скляній колонці. Змінними параметрами були також значення pH модельного розчину (6.0; 7.0 і 8.5) і температура (15, 20, 25 і 30 ºC). Встановлено, що значення константи швидкості збільшувалось не тільки зі збільшенням температури і витрати повітря, але й із збільшенням pH середовища. Збільшення pH середовища спричиняє зменшення редокс-потенціалу окисника, проте водночас сприяє зміщенню рівноваги в системі* H_2S*–*HS^- *у бік йонної форми сірководню. Це забезпечує більшу швидкість його окиснення. Розраховані значення температурного коефіцієнта Вант Гоффа (2.0…3.7) і енергії активації окиснення* H_2S *(53…67 кДж/моль) свідчать про перебіг процесу у кінетичній області. Встановлено, що за pH від 7.0 і вище за витрати повітря близько 200* $см^3$*/хв (за умов досліду) ступінь окиснення сірководню впродовж 60 хв прямує до 100 %. Отже, виконаними дослідженням підтверджено високу ефективність отриманого сорбенту, модифікованого частинками* Mn_xO_y*.*

Ключові слова: *клиноптилоліт, мангану оксиди, модифікування, очищення води, сірководень, сорбція*