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FORMATION OF SULPHIDE AND ITS CHEMICAL EQUILIBRIUM IN SEWAGE PIPES. INFLUENCE OF H_2S TO AEROBIC MICROORGANISMS OF ACTIVATED SLUDGE

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The objective of this work was to study the sulphide, especially the dihydrogen sulphide formation process in sewage pressure pipes and the influence of sulphur rich wastewater on oxygen consumption of activated sludge of Kohtla-Järve wastewater treatment plant (WWTP). In this work the equilibrium distribution between three different forms of sulphide was investigated by changing pH of the wastewater and Na_2S solutions in the closed vessel. At the same time the content of H_2S in the gas phase was measured. To estimate the influence of H_2S on the aerobic microorganisms of activated sludge, the ISO 8192 standard test of inhibition of oxygen consumption by activated sludge has been used. At the same time, other inflows of Kohtla-Järve WWTP have been investigated.

The leachate from semicoke and ash heaps, rich in sulphates and sulphides (pH 10–12) did not cause any significant inhibition of oxygen consumption of activated sludge microorganisms. The wastewater from oil shale chemical industry containing sulphates and sulphides (pH around 6–6.5), and also gross inflow of Kohtla-Järve WWTP, cause inhibition of oxygen consumption of activated sludge.

Introduction

The sulphide formation as a result of reduction of sulphate by the sulphate-reducing bacteria *Desulphovibrio* and *Desulphotamaculum* [1] is a common process in the sewage collection systems. The intensity of sulphide formation depends on several parameters of sewage, such as the content of organic compounds, sulphate concentration, pH, dissolved oxygen, etc.

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Significant physical factors are temperature, flow velocity, wastewater retention time and the surface area inside the pipe where slim layer is formed [2, 3]. The highest rate of sulphide formation is found to be within the pH range of 6.0 to 8.5 [4, 5].

The sulphide formation process in sewage pipes and wastewater streams can be described by the equation [6]:

$$SO_4^{2-} + 8H^+ + 8e^- \rightarrow S^{2-} + 4H_2O \tag{1}$$

This reaction does not occur, if dissolved oxygen or other strong electron acceptors, e.g. nitrate, are present in wastewater [7]. Organic matter in the wastewater could be oxidized in anaerobic conditions as well (e.g. in the anaerobic part of a slim layer formed on the wall of wastewater collecting pipe) using sulphur as terminal electron acceptor. As a result of this process sulphur will be reduced to sulphide which, depending on the pH of wastewater, can occur in three different forms (Fig. 1): sulphide ion (S^{2-}), hydrogen sulphide ion (HS^-), and dissolved dihydrogen sulphide (H_2S) [8, 9]. Dihydrogen sulphide is toxic to aerobic organisms of wastewater, when appearing in the air (evaporated from wastewater during aeration), it is dangerous to human already at very low concentrations [10–12].

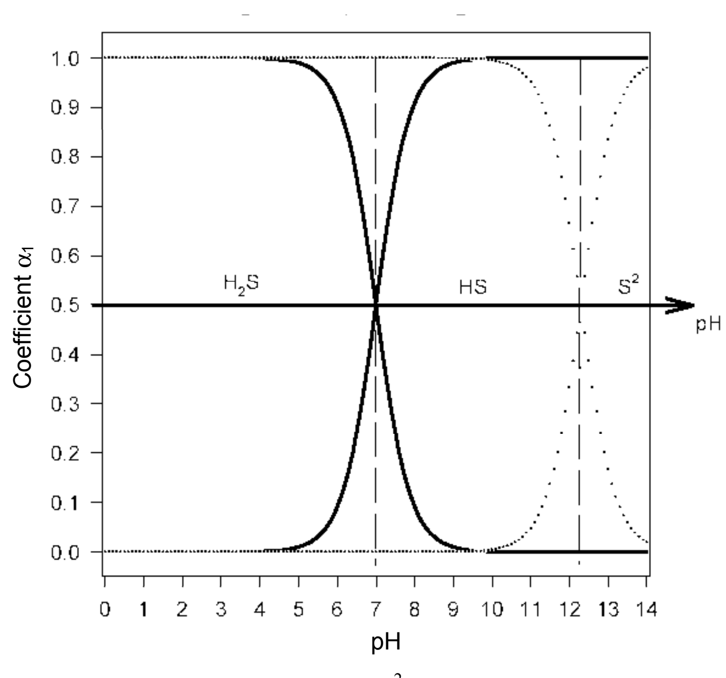

Fig. 1. The occurrence of sulphide (S^{2-}), hydrogen sulphide (HS^-), and dissolved dihydrogen sulphide (H_2S) in the water, depending on water pH value [13]; $pK_1 = 7$, $pK_2 = 12.3$

Results and Discussion

The objective of this work was to study the sulphide formation process in the pressure pipes and the influence of sulphur-rich wastewater on oxygen consumption of activated sludge of Kohtla-Järve WWTP. Kohtla-Järve with its surroundings is a main industrial district of Estonia producing different chemicals. Some of enterprises in the district are using oil shale as raw material. Wastewaters from oil shale and other chemical industries have a high concentration of sulphate and low pH (6–8). Leachate from semicoke heaps (formed as a result of oil shale chemical industry) is also directed to Kohtla-Järve WWTP for treatment, and those wastewaters are also rich in sulphur and phenols. Except for municipal wastewater and wastewater from Nitrofert (producing fertilizers), all wastewaters entering Kohtla-Järve WWTP are causing problems to the wastewater treatment and surroundings due to their high sulphate content and pH. In this study different aspects of sulphur-rich wastewater collection and treatment are investigated.

Sulphide Formation and Occurrence Depending on pH

The sulphide formation in the 16 km long pressure pipe, where the wastewater retention time is 24 hours, has been investigated. Sulphate content of wastewater entering the pipeline was measured 443 mg/l (average value for 24 h) at pH 7 and sulphide concentration 34 mg/l. During the stay in pipeline parameters of wastewater changed as follows: sulphate content decreased by 25 %, sulphide concentration increased by 4 mg/l (11%), and pH decreased by one unit (from 7 to 6). Biochemical oxygen demand (BOD) was decreased by 10% during the stay in pipeline. Mass balance for sulphur showed sulphur loss in pipeline that can be explained by the emission of dihydrogen sulphide to the atmosphere at the end of pipeline at entering the collector chamber of WWTP. As seen from Fig. 1, at pH 6 (wastewater outlet from pipeline) 90% of the sulphide is in the form of H_2S, and it leaves the dissolved phase of the wastewater due to the decrease of pressure at entering the collector.

For estimation of the amount of H_2S formed in anaerobic pipelines at different pH values, the distribution between different forms of sulphide and H_2S emission rate from liquid phase to gaseous one was studied. Content of H_2S in the gaseous phase in the closed agitated flask (total volume of 3,300 ml) was measured with gas detector GA 2000 (Geotechnical Instruments) [14]. The concentration of the total sulphides ($H_2S + HS^- + S^{2-}$) in liquid phase (volume 300 ml) was determined iodometrically. For pH measurement the HANNA HI 991000 pH/Temperature Meter was used. The results of an experiment of stepwise acidification of Na_2S solution with sulphuric acid are shown in Fig. 2. At pH 9.6 at the beginning of the experiment sulphide content in the liquid phase was 1.86 mg HS^-, and no H_2S was detected in the gaseous phase. The maximum H_2S content of the gas phase at pH 3.4 was 175 ppm and the sulphide content of the liquid phase at the same time was 1.05 mg. Calculating the value of sulphide concentration in the liquid phase from equilibrium data, it was shown that the calculated and measured data differed only by 2.5 %

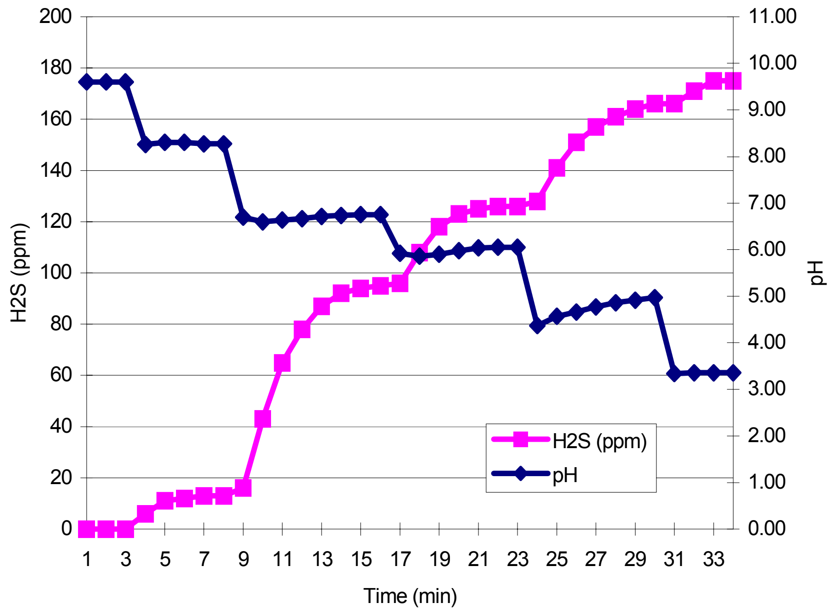

Fig. 2. H_2S content of the gaseous phase in the experiment of stepwise acidification of Na_2S solution with sulphuric acid in closed vessel

The results show that after changing pH of the solution H_2S content of the gaseous phase above the Na_2S solution stabilizes after 6–7 minutes (equilibrium state between two phases). At pH value 7.3 (typical value for mixed wastewater inflow of Kohtla-Järve WWTP) 48% of the sulphide exist in the form of H_2S. In the case of open systems at lower pH values (7 and less), where the content of H_2S in the atmosphere is near to zero, all the sulphide in the form of H_2S will continuously move from the liquid phase to the air causing toxicity and smell problems for surroundings because due to the wind the gaseous H_2S escaped from the water will spread over the landscape and the town around Kohtla-Järve WWTP. This problem is still unsolved in the wastewater inflow area in Kohtla-Järve WWTP.

Standard Test for Estimation of Inhibition of Oxygen Consumption of Activated Sludge Microorganisms (ISO 8192)

The other aspect of the study was to estimate how dihydrogen sulphide (H_2S) affects the oxygen consumption of aerobic organisms present in activated sludge of Kohtla-Järve WWTP. In this study the ISO 8192 standard test has been used to estimate the inhibition of oxygen consumption of activated sludge microorganisms [15].

The test is suitable for estimating the toxicity of wastewater to activated sludge organisms. Based on the test results, the inhibition rate of oxygen consumption and the concentration of wastewater, which causes inhibition of 50% of oxygen consumption of activated sludge organisms (EC 50), can be calculated.

In the tests different wastewaters of different concentrations were used, and the inhibition of oxygen consumption (%) has been calculated (Formula (2)):

$$I = \frac{R_B - (R_T - R_{PC})}{R_B} \times 100 \qquad (2)$$

where R_T – oxygen consumption rate of tested wastewater;

R_B – oxygen consumption rate of blank mixture (control, without wastewater);

R_{PC} – physical-and-chemical oxygen consumption rate of tested wastewater (vessel without activated sludge).

Leachate from Semicoke Heaps

The content of leachate reaching Kohtla-Järve WWTP depends on seasons. In 2002, the average sulphate concentration was 535 mg/l and sulphide concentration 45 mg/l. Average pH value was 11.3. At high pH values the sulphide in leachate does not occur as dihydrogen sulphide (H_2S), and sulphides in wastewater are not toxic for mixed bacterial communities of activated sludge. The inhibition of oxygen consumption rate of activated sludge microorganisms by the leachate containing 20 mg/l sulphide was estimated at three different pH values. The maximum sulphide concentration obtained after dilution of studied leachate was 7.5 mg/l.

As shown in Fig. 3, the oxygen consumption rate was increased at all sulphide concentrations (7.5 mg/l) compared with oxygen consumption rate of the blank (control) sample. During the tests vessels were closed to avoid volatilisation of gases from study environment. The results of the inhibition test are presented in Fig. 3. As seen from the data, all studied amounts of wastewater (by increasing the amount of wastewater the concentration of sulphides in test media is increasing accordingly) gave negative inhibition values of oxygen consumption, which is decreasing with increasing the amount of wastewater. The decrease in the negative value of the inhibition of oxygen consumption is connected with higher sulphide concentrations due to the added wastewater quantity.

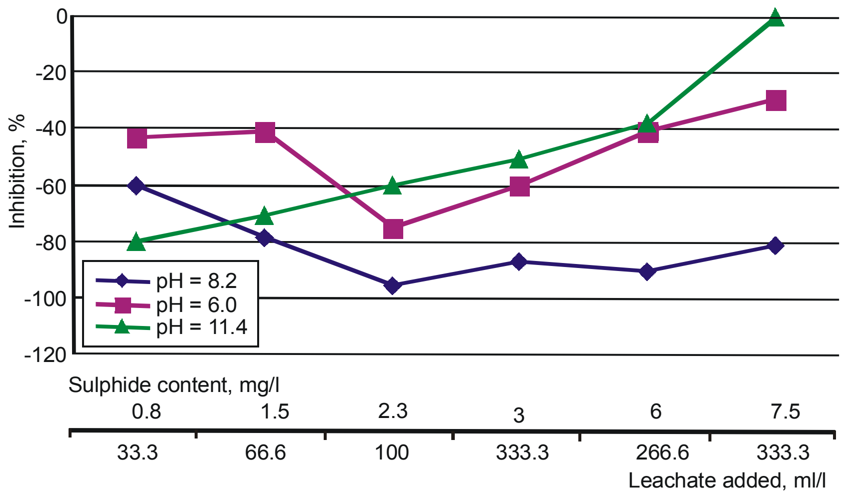

Fig. 3. Inhibition of oxygen consumption rate of activated sludge leachate of semicoke heaps at three different pH values (6.0, 8.2 and 11.4) and different sulphide concentrations

Wastewater from Oil Shale Chemical Industry

Wastewater from oil shale chemical industry has high sulphide content (135 mg/l) and low pH value (5–5.5) before neutralization. After neutralization the value of wastewater pH will be 6–6.5. Wastewaters used in inhibition tests of oxygen consumption of activated sludge had pH 5.0 and 6.3. As shown in Fig. 4, the EC50 value for wastewater with pH 5.0 was found 24 mg/l (sulphide concentration). In the case of wastewater with pH 6.3 it was possible to estimate the EC40, and it was found to be 45 mg/l.

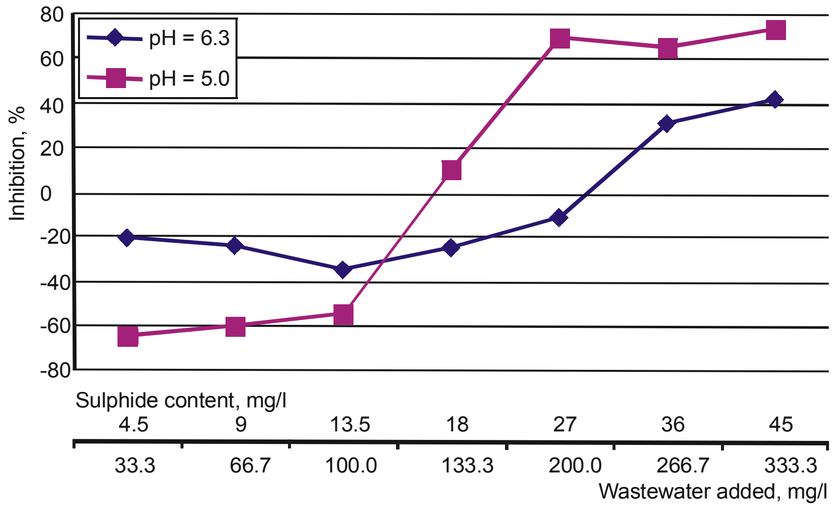

Fig. 4. Inhibition of the oxygen consumption rate of activated sludge by wastewater from oil shale chemical industry at pH values 5.0 and 6.3

Inflow from Kohtla-Järve WWTP

After mixing different wastewater streams coming from industry, households and semicoke heaps and before biological treatment in Kohtla-Järve WWTP, the average sulphide concentration of wastewater was 39 mg/l and pH 7.3. As the wastewater purification process at the first stage of the Kohtla-Järve WWTP was not effective, the inhibitory effect of the mixed wastewater to oxygen consumption of activated sludge of the plant has been studied.

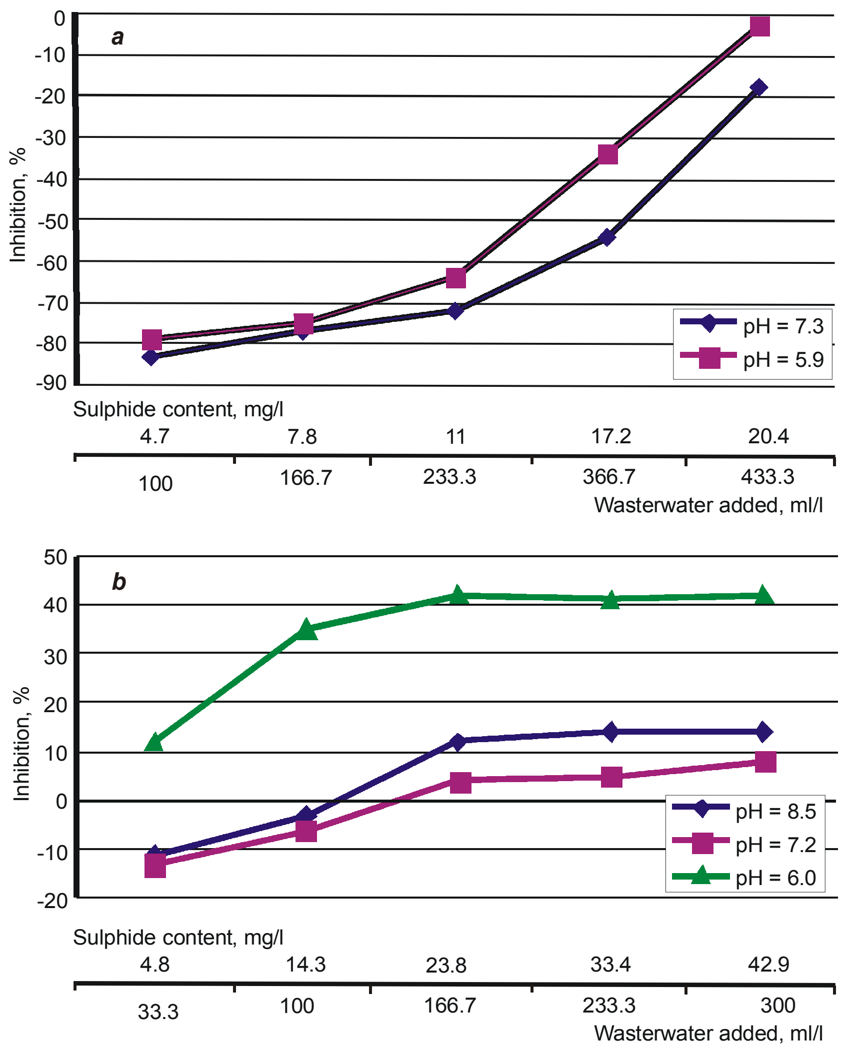

Fig. 5. Inhibition of the oxygen consumption rate of activated sludge by inflow of Kohtla-Järve WWTP at pH values: (*a*) 5.9 and 7.3; and (*b*) 6.0, 7.2 and 8.5

Figure 5 presents the results of testing the inhibiting effect of wastewater on oxygen consumption of activated sludge by changing pH and sulphide content of the wastewater. The sulphide content of the studied wastewater was 47 mg/l and pH was 7.3. As seen from the results, low sulphide concentrations did not inhibit the oxygen consumption, even at lower pH values (Fig. 5*a*). To study the toxicity of sulphides to activated sludge microorganisms, the sulphide concentration in the added wastewater was increased. The maximum sulphide concentration in the test media in experiments was 42.9 mg/l. As seen from Fig. 5*b*, in this case some inhibition of oxygen consumption occurs at all investigated pH values. It is seen that higher sulphide content at lower pH values substantially inhibits the oxygen consumption rate of activated sludge and can decrease the efficiency of wastewater treatment process in Kohtla-Järve WWTP. At higher pH values the inhibition of activated sludge is observable only at higher sulphide concentrations.

For assessing the potential toxicity of sulphide to oxygen consumption of activated sludge, measurements of oxygen consumption rate with sulphide-free wastewater were performed. For the experiment the influent wastewater of Kohtla-Järve WWTP was purified from sulphides (blowing oxygen through the wastewater at low pH), and different amounts (10–80 ml) of sulphide-free wastewater at pH 7.3 were added to the test media. The results of the test are shown in Fig. 6. As seen from the results, the rate of oxygen consumption of activated sludge in the measuring vessel is increasing when adding sulphide-free wastewater into the test media. The performed tests showed no inhibition in the samples where the sulphide-free wastewater was added.

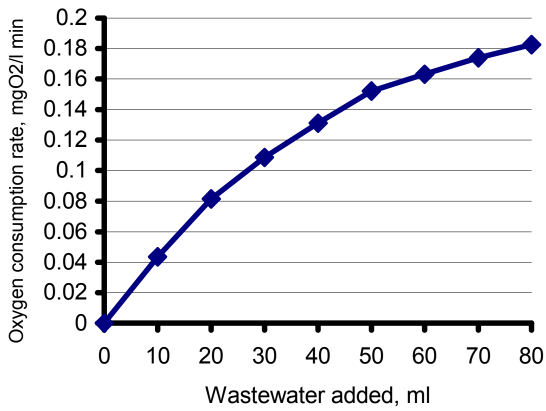

Fig. 6. Influence of added sulphide-free wastewater on oxygen consumption rate by activated sludge microorganisms

Performing inhibition tests with wastewaters another problem will arise concerning the amount of organic matter (substrate) in the test vessels. Using higher amounts of wastewater leads to higher concentrations of organic matter in the vessels, and that will influence the oxygen consumption process. To eliminate the influence of substrate content of the wastewater on the oxygen consumption processes, experiment with the same amount of sulphide-free wastewater (30 ml in each vessel) was performed varying the sulphide content adding different amounts of Na_2S solution. The test was performed at pH 6, and the results are presented in Fig. 7.

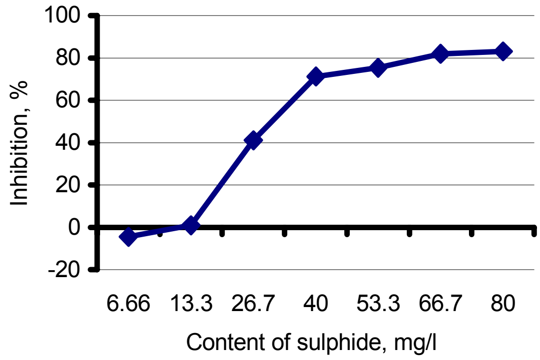

Fig. 7. Inhibition of oxygen consumption of activated sludge by sulphide-free inflow of Kohtla-Järve WWTP where sulphide is added as Na_2S solution

The results show that some stimulation in oxygen consumption occurs at sulphide concentrations below 13.3 mg/l. All higher concentrations of sulphide cause inhibition of oxygen consumption, and EC50 value of the wastewater is 29 mg/l.

Conclusions

Sulphide formation from sulphates, generated by microorganisms, is a prevalent process in anaerobic sewage collection systems. After sulphate is consumed as electron acceptor, the sulphide is released to the wastewater where it distributes between three forms – sulphide ion (S^{2-}), hydrosulphide ion (HS^-) and dissolved dihydrogen sulphide (H_2S_{aq}). In the presence of gaseous phase the dissolved dihydrogen sulphide (H_2S_{aq}) will move from the liquid phase to the gaseous one (H_2S_g).

The results of the study show that the change in wastewater pH causes the change in equilibrium between different forms of sulphide in the liquid phase, as well as a rather quick transfer of gaseous H_2S from the liquid phase into the gaseous one (in the performed experiments in 7–10 minutes). Intensive turbulence (aeration in wastewater treatment) accelerates achieving the equilibrium distribution of H_2S between the gaseous and liquid phases. In pressurized sewage pipelines H_2S does not exist in the gaseous phase but the emission process will occur rapidly at the outlet of pipes due to the relatively high turbulence. In equilibrium between wastewater and open atmosphere H_2S is permanently transferred across water – air interface to the air causing toxic effect and odor problems to the environment. Due to continuously shifting equilibrium the sulphides could be completely removed from wastewater.

Wastewaters from different streams in the Kohtla-Järve area, containing sulphates and sulphides and having fluctuating pH (frequently being below 7), are causing the inhibition of oxygen consumption of the activated sludge. The reason of toxicity of wastewater is dissolved dihydrogen sulphide at lower pH values. Even at pH 7.0 the share of toxic H_2S in wastewater is 50% of sulphides present. Concentration of H_2S in wastewater will increase with decreasing pH. The results of the present study showed the inhibition of oxygen consumption of activated sludge at the concentration of sulphide 11 mg/l at the pH value 7.3.

Sulphur-rich wastewaters in the Kohtla-Järve district influence the efficiency of wastewater treatment process and, due to the sulphide formation and varying pH of wastewater, may cause a serious toxic effect to the surrounding environment.

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