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Wastewater treatment from hydrogen sulphide using iron-containing coagulant

Abstract: The increase of sulphate content in natural water sources due to anthropogenic causes leads to a corresponding increase of sulphate and sulphide concentrations in wastewater. Biochemical reactions occurring in sewage systems of sulphate reduction to sulphides and their subsequent oxidation to sulphuric acid cause microbially induced acid corrosion of concrete pipes. In addition, biochemical processes occurring in wastewater are accompanied by the release of toxic gases, including hydrogen sulphide, which adversely affect the human body. The methods based on the binding of hydrogen sulphide into insoluble metal sulphide are recognised as promising for the treatment of sulphide-containing waters. For the realisation of the process, it is offered to use iron compounds as the least toxic and relatively cheap reagents. The complex coagulant based on ferric diatomite, sodium ferrite and iron compounds for the treatment of wastewater from hydrogen sulphide is developed. Test tests of iron-containing coagulant have been carried out: at a flow rate of sewage 2.73 m³/hour, optimal dose of reagent 90 mg/l the concentration of hydrogen sulphide in treated water is 1.07 mg/l, which is close to the maximum permissible concentration (MPC) values for sewage - 1 mg/l.

Keywords: wastewater, diatomites, industrial applications, dry mixes, foam glass, iron oxide pigments

Introduction

At present, there is a tendency to increase the sulphate content in natural water sources, which leads to a corresponding increase in the concentration of sulphates and sulphides in wastewater. Hydrogen sulphide-induced corrosion of concrete sewer pipes is a serious problem for water utilities worldwide (Zhang et al., 2008; Hvitved-Jacobsen et al., 2013; Pikaar et al., 2014; Aminuddin et al., 2024).

The content of hydrogen sulphide and sulphides in waters due to their toxicity is standardised: the MPC of hydrogen sulphide for water bodies of household and drinking and domestic water use is 0.05 mg/dm³, for wastewater sent for biological treatment - 1 mg/l, for the air of settlements, is 0.008 mg/m³.

There are various methods of neutralisation of hydrogen sulphide dissolved in sewage: physical-chemical, chemical and biological. In several works for removal of hydrogen sulphide natural diatomite and iron compounds were used (Simon et al., 2002; Majeda et al., 2004; Wu et al., 2005; Sun et al., 2013; Myrzaliev et al., 2021; Ospanov et al., 2022).

Physico-chemical methods based on separation from the water of molecular hydrogen sulphide in a gas phase under appropriate conditions, for example, by the creation of the big surface of the interface (film degassing), increase of temperature of water (thermal deaeration), lowering of pressure to a level at which water boils without additional heating (vacuum degassing).

In waters with pH>8.5 hydrogen sulphide is mainly in the form of sulphide and hydrosulphide and for its transfer in molecular form for the subsequent degassing it is necessary to acidify water to pH 5 and below. A negative side effect is the release of hydrogen sulphide into the atmosphere.

Chemical (reagent) methods of hydrogen sulphide extraction with its subsequent utilisation in the form of sulphur-containing precipitates are based on oxidation of sulphides to elemental sulphur by oxidising reagents (oxygen, ozone, hydrogen peroxide, chlorine, chlorine dioxide, sodium hypochlorite, chlorine lime, iodine, manganese dioxide, potassium permanganate). To extract sulphur from water, sedimentation, filtration, and flotation are used. The reagents used require high specific consumption, many of them require special safety measures during their storage and use. The main disadvantages of using oxidising reagents are associated with secondary contamination of aqueous solutions with manganese compounds, chlorides and peroxides, which harm the environment. Methods of chemical precipitation of hydrogen sulphide are based on its property to form water-insoluble sulphides with the majority of metals. In practice the method is realised by treatment of water with iron-containing coagulants, as a result of interaction with which iron sulphide insoluble in water is formed, accumulated in special settling tanks. It is concluded that methods based on the use of iron-containing reagents are one of the promising ones for the removal of hydrogen sulphide from wastewater.

Removal of sulphides from oil refinery wastewater by chemical precipitation has been investigated (Ren et al., 2021; Kenzhaliyev et al., 2021; Myrzaliev et al., 2022). Wastewater samples were taken from the treatment facilities of an oil refinery. Physicochemical treatment of industrial wastewater was carried out using conventional coagulants $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and alkaline reagents $\text{Ca}(\text{OH})_2$ and CaCO_3 , which were applied to both untreated wastewater and model wastewater, with the addition of sulphides. Sulphide removal efficiency (96-99 %) was achieved when Fe^{2+} ions were used together with $\text{Ca}(\text{OH})_2$ as an auxiliary precipitant.

Studies on the removal of S^{2-} ion from sodium aluminate solutions by sodium ferrite have been carried out (Li et al., 2016). The synthesis of sodium ferrite and its behaviour in sodium aluminate solutions containing S^{2-} have been described. The desulphurisation rate can reach about 70 % within 60 min. at a molar ratio of iron to sulphur of 1:1 to 1.5:1. The efficiency of the process depends on the activity of $\text{Fe}(\text{OH})_3$ formed during the hydrolysis of sodium ferrite.

The synthesis of a reagent containing alkali metal ferrates and alkali is described in (Orekhova A.I. et al., 2014). The main components of the reagent are potassium ferrate K_2FeO_4 (25.2-40.3 wt.%) and alkali KOH (47.2-68.1 wt.%). It was found that the high oxidising ability of the reagent is related to the presence of ferrate, and high adsorbing ability - to the formation of a highly dispersed precipitate of iron (III) hydroxide.

Composite inorganic coagulants are mixtures of inorganic aluminium- and iron-containing coagulants. Composite reagents are produced by mixing individual components, processing of mixed raw materials or production waste. The use of the latter allows to additionally solve environmental problems related to waste utilisation.

Thus, iron compounds are estimated as one of the most effective for neutralisation of hydrogen sulphide in wastewater. Speed and completeness of process of interaction of dissolved hydrogen sulphide with iron compounds to a great extent is determined by a form of finding of iron hydroxides in water solutions. As effective desulphators can be considered composite iron-containing reagents.

Research Methods

The following methods of analysis were used to determine the composition of the initial raw materials and the obtained products: mineralogical, chemical, colorimetric X-ray phase, and X-ray fluorescence. Equipment: atomic emission spectrometer Optima 2000 DV; X-ray diffractometer D8 Advance BRUKER, Cu α -radiation; X-ray fluorescence spectrometer Venus 200 PANalytical B.V.

Analyses were carried out according to the method of measuring concentrations of hydrogen sulphide in wastewater by photometric method. The method is based on the interaction of hydrogen sulphide and sulphides with products of oxidation of N, N-dimethyl-p-p-phenylenediamine with iron (III) salt with formation of methylene blue, extraction of the obtained dye with chloroform in the presence of sodium dodecyl sulfate and measurement of optical density of the coloured solution at a wavelength of 656 nm.

Research Results

The experimental setup was mounted at the canal after the grate up to the sand trap. The scheme of the installation is presented in Figure 1. The capacity of the installation was 2.73 m³/hour.

The unit worked in the following mode: Wastewater after the grid from the canal with the help of pump (1) goes to the tank (2) with a constant head. A 227-litre iron barrel was used as a tank. The reagent flow rate is regulated using a gate valve. Then the wastewater is directed to the mixer (3), where the solution of complex iron-containing reagent and air are supplied. The sketch drawing of the mixing tank is given in Appendix A. Preparation of the solution of complex iron-containing reagent takes place in the solution tank (4), where the necessary amount of dissolved reagent is loaded. Air is supplied to the mixer by compressor (5). In the mixer, the wastewater is mixed with the reagent, and then enters the flaking chamber (6), where coagulation takes place under the influence of the reagents added to the wastewater. A sketch drawing of the flaking chamber is given in Appendix A. After the flaking chamber, the water enters the settling tank (7), where the wastewater is stabilised and the flake sludge settles to the bottom, while the treated water flows into the canal.

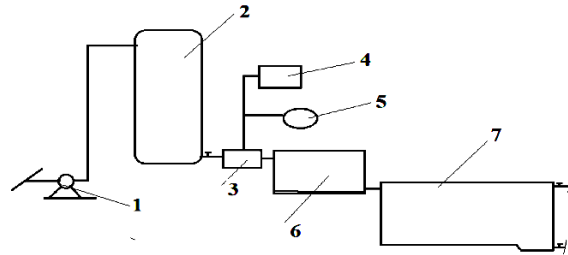


Figure 1. Schematic diagram of the experimental setup

There were 15 experiments of 1-2 days duration on 3 modes of operation of the experimental unit.

Mode 1: Wastewater flow rate 2.73 m³/hour, dose of complex iron-containing reagent 40 mg/l.

Mode 2: Wastewater flow rate 2.73 m³/hour, dose of complex iron-containing reagent 90 mg/l.

Mode 3: Wastewater flow rate 2.73 m³/hour, dose of complex iron reagent 120 mg/l.

Preparation of the solution of complex iron-containing reagent took place in the solution tank, where the necessary amount of reagent and clean tap water was loaded.

The experimental unit was operated in flowing mode, wastewater flow rate was measured by volumetric method. The residence time of wastewater in the mixer was 2 min, in the flaking chamber - 30 min., in the settling tank - 60 min. Samples for analysis were taken after the tank as source water and after the settling tank as treated water. Sampling was done manually according to general rules.

Water chemistry analyses were performed for the following parameters: suspended solids, phosphate, iron, hydrogen sulphide, sulphate and pH. Each series corresponded to different technological regimes; the dose volume of complex iron-containing reagents was changed.

The results of wastewater analysis after coagulant application for the following parameters: suspended solids, phosphates, iron, hydrogen sulphide, sulfates and pH depending on the dose of complex iron-containing reagent are shown in Table 1, Figures 2 - 4.

Table 1. Summarised results of the test trials

Name of indicators	pH	Hydrogen sulphide	Suspended solids	Phosphates	Iron	Sulphates
1 mode: Wastewater flow rate 2.73 m ³ /hour, dose of complex iron-containing reagent 40 mg/l.	7.5	<u>3.52</u>	<u>439.0</u>	<u>10.2</u>	2.53	52.0
	7.4	2.65	309.0	6.3	3.83	67.5
		E = 24.6 %	E = 29.6%	E = 38.2%		
2 mode: Wastewater flow rate 2.73 m ³ /hour dose of complex iron-containing reagent 90 mg/l.	7.7	<u>3.52</u>	<u>302.0</u>	<u>4.3</u>	2.95	79.2
	7.6	1.07	192.0	0.2	4.16	94.2
		E = 69.6 %	E = 36.4%	E=95.3%		
3 mode: Wastewater flow rate 2.73 m ³ /hour, dose of complex iron-containing reagent 120 mg/l.	7.6	<u>3.52</u>	<u>289.6</u>	<u>3.4</u>	2.07	106.6
	7.5	1.59	175.0	0.2	5.94	261.9
		E = 54.8 %	E = 39.6%	E = 94.1%		

Note: in the numerator source water, in the denominator treated water; E - efficiency of wastewater treatment from chemical compounds and suspended solids.

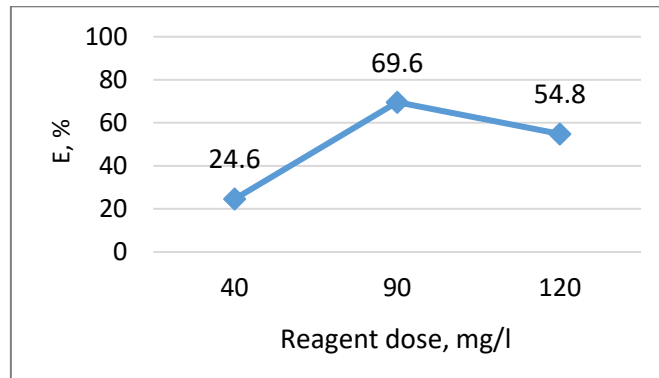


Figure 2. Reduction of hydrogen sulphide content in wastewater depending on the dose of iron-containing reagent

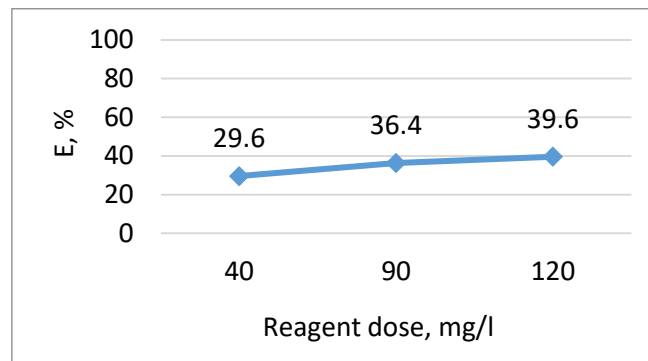


Figure 3. Reduction of suspended solids in wastewater depending on the dose of iron reagent on the dose of iron-containing reagent

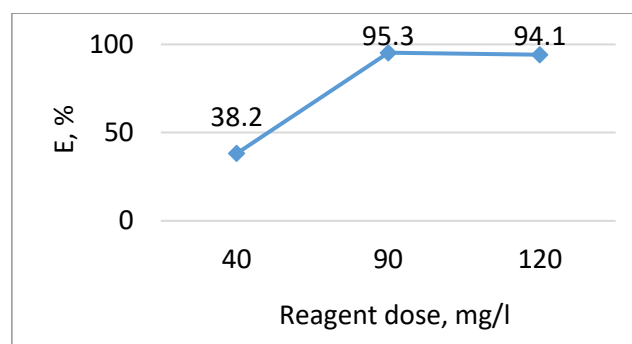


Figure 4. Reduction of phosphate content in wastewater depending on the dose of iron reagent on the dose of iron-containing reagent

Thus, by the results of test tests of complex iron-containing reagent, it is concluded that for treatment of wastewater from hydrogen sulphide it is expedient to use complex iron-containing reagent. The best indicators of clearing from hydrogen sulphide are reached on experimental installation at a flow rate of wastewater 2.73 m³/hour, optimum dose of complex iron-containing reagent 90 mg/l - average value of concentration of hydrogen sulphide in initial water made 3.52 mg/l, in treated water – 1.07 mg/l. Reduction of hydrogen sulphide concentration made 69.6 %.

The best performance of phosphate purification was achieved at the experimental unit at the wastewater flow rate of 2.73 m³/hour, the optimal dose of complex iron-containing reagent 90 mg/l - the average value of phosphate concentration in the source water was 4.3 mg/l. and in treated water - 0.2 mg/l. The reduction of phosphate concentration was 95.3 %.

Conclusion

The method of obtaining complex coagulants is proposed. As initial components sodium ferrite-aluminate, natural ferruginous diatomite and technical iron sulfate are used. Sodium ferrite-aluminate is produced based on waste alumina production of ferruginous sands by sintering with soda ash at 1000-1100 °C. The ratio of initial components is determined experimentally depending on the composition of the wastewater. Technological parameters of the application of complex coagulants in the process of wastewater treatment from hydrogen sulphide are developed. Experiments with 3 modes of operation of the experimental unit have been carried out. The residence time of wastewater in the mixer was 2 min, in the flaking chamber 30 min, and in the settling tank 60 min. Experimentally it is established that the optimum consumption of complex iron-containing reagents at removal of hydrogen sulphide and phosphates is 90 mg/l. The method of reception of complex iron-containing reagents for the treatment of wastewater from hydrogen sulphide is economical due to the use of accessible raw sources.

CRedit author statement: **S. Temirova:** Conceptualization, Methodology, Validation, Writing draft preparation; **D. Fischer:** Data curation, Visualization, Investigation; **Ye. Kuldeyev:** Supervision, Reviewing, Software, Editing.

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