Integrated sulfide alkali wastewater treatment using spent galvanic solutions

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Abstract. We identified the efficiency of spent Ni²⁺-containing galvanic solutions for removing sulfide ions from sulfide alkali wastewater. It was found that the removal of sulfide ions led to achieving 89.7 % of purification degree by the chemical oxygen demand value. We also studied how various concentrations of nickel (II) and copper (II) ions affect the oxidation intensity of pollutants in mixed wastewater with ambient oxygen and with ozone-air mixture. Optimal conditions were identified for cleaning sulfide alkali wastewater from hydrocarbons: Oxidation of organic components by ozone-air mixture for 30 minutes, containing 300 mg/dm³ of nickel (II) ions; implementing such conditions resulted in the greatest reduction of the chemical oxygen demand value (down to 798 mg of O/dm³). A comprehensive method for the purification of sulfur-alkaline wastewater is proposed, which includes the stages of removing readily volatile hydrocarbons by simple distillation, sulfide ions by reagent deposition using spent Ni²⁺-containing galvanic solutions, and soluble hydrocarbons by oxidation of ozone-air mixture with adding 300 mg/dm³ of nickel (II) ions contained in galvanic wastewater. Implementation of this technique led to achieving 96% of the wastewater purification degree by the chemical oxygen demand value, which allows discharging wastewater into biological treatment.

Recently, great attention is being paid to the problem of the chemical industry wastewater treatment. This is because such wastewater contains toxic substances that, if not removed completely, may lead to creating unfavorable environmental conditions in natural water bodies [1]. Environmentally detrimental substances are also formed as a result of machine-building production [2, 3], including using ceramic, polymer and metal powders in the trending additive processes [4-7]. However, the most hazardous to the environment is sulfide alkali wastewater (SAWW) produced by chemical industries. Since this wastewater contains pollutants, such as biologically persistent organic substances, including benzene, toluene, naphthalene, etc., and sulfurous compounds, this affects detrimentally the biochemical regime of water bodies, as well as the vital activities of aquatic biocenos [8-10].

Experiences in operating biological treatment plants (BTPs) at enterprises show that, even when complying with the regulatory requirements for mixed wastewater to be fed to standard BTPs with the existing set of processing units and with the optimal operation parameters retained, it is impossible to ensure the threshold limit values for fishery water bodies [11]. In this regard, developing new efficient techniques of local SAWW treatment is a relevant research-engineering problem.
Literature analysis has shown that using mechanical methods involving advanced hardware [12, 13] is only efficient in removing insoluble hydrocarbons, and applying them is only reasonable at the pre-treatment stage.

Using extraction, membrane, adsorption, flotation or coagulation techniques in the practice of SAWW treatment is characterized by high capital and operating costs due to the need for implementing chemical storage areas, formation of hardly recyclable precipitates, and high power consumption [14].

The authors of the works [15, 16] studied the possibility of using SAWW as a reagent to extract metal ions from galvanic wash wastewater, which showed the high efficiency of the method used. However, this cleaning results in secondary contamination with toxic hydrocarbons contained in SAWW. Moreover, results of these studies showed that a small amount of SAWW is required to clean wastewater from metal ions, which does not allow disposing it in the resulting volumes.

Chemical cleaning of SAWW from hydrocarbons using oxidants is the most preferable due to its efficiency, environmental friendliness, and easy process automation [8-11, 14, 17-21].

Using Ni$^{2+}$- and Cu$^{2+}$-containing spent galvanic solutions (SGSes) as reagents and catalysts in depositing sulfide ions and oxidizing soluble hydrocarbons will also reduce the cost of treating the water studied and eliminate the use of additional reagents.

Considering the complex composition of the wastewater under study, i.e., floating and soluble hydrocarbons and sulfide ions, not without interest was to investigate cleaning it using an integrated technique that includes sequentially removing readily volatile hydrocarbons by simple distillation, sulfide ions by reagent deposition with SGSes, and soluble organic compounds by catalytic oxidation with ozone-air mixture and ambient oxygen and with adding nickel (II) and copper (II) ions that are part of the SGS.

This study was aimed at determining the efficient conditions for cleaning of SAWW from hydrocarbons and sulfide ions, using Ni$^{2+}$- and Cu$^{2+}$-containing SGSes.

In this paper, the research object is SAWW formed in washing pyrolysis gases to remove hydrogen sulfide and carbon dioxide when manufacturing ethylene, as well as Ni$^{2+}$- and Cu$^{2+}$-containing SGSes.

Based on the fact that most of the organic contaminants of SAWW are highly toxic, biochemically hard-to-oxidize benzene (51.4%) [20], considering the small amounts discharge and its high temperature, and aiming at recovering benzene and reducing the chemical oxygen demand (COD) value, a simple distillation was performed until distillate is obtained in the amount of 0.5% of the fluid at the first stage of study.

To further remove sulfide ions by depositing at the second stage of our study, spent Cu$^{2+}$- and Ni$^{2+}$-containing SGSes were being added until precipitate stopped being formed.

Pollutants in SAWW that has passed the stage of simple distillation and deposition of sulfide ions, were oxidized at the temperature of 20±1° C at a laboratory plant consisting of a compressor, air purification unit, ozone generator, and oxidation reactor [21]. Sparging with ambient air was performed at the same plant, but no voltage was applied to the ozone generator.

During the control experiment, 100 ml of pre-treated wastewater were poured into the oxidation reactor, and we sparged ambient oxygen with a flow rate of 80 l/h or ozone air mixture (OAM) with the same flow rate and ozone concentration of 3 mg/l during 30 minutes.

COD and alkalinity values were found in the selected samples after 5, 10, 20, and 30 minutes of treatment with oxidant.

Experiments on catalytic oxidation of the SAWW components differed from the control one by only added Ni (II) and Cu (II) ions contained in the SGS.

This present study of SAWW treatment is a continuation of works [17, 19]. The main difference of the process solution of the SAWW under research from that proposed previously consists in excluding the preliminary stage of its neutralization with sulfuric acid, which, in turn, contributes to preventing the release of considerable hydrogen sulfide amounts into the atmosphere, as well as reducing the amounts of sulphate ions in water.
At the initial stage of SAWW treatment, a simple distillation was performed followed by depositing sulfide ions with Ni(II) and Cu(II) ions contained in SGS. Results of SAWW treatment after simple distillation and depositing sulfide ions are shown in Table 1.

Table 1. Results of SAWW treatment after simple distillation and depositing sulfide ions with Ni(II) and Cu(II) ions contained in SGS.

| SAWW treatment indicators | Initial SAWW | Distillation | Depositing sulfide ions with Ni (II) ions in the volumetric ratio of SGS:SAWW = 1:1.37. | Depositing sulfide ions with Cu (II) ions in the volumetric ratio of SGS:SAWW = 1:1.94 |
|---------------------------|--------------|--------------|-------------------------------------------------|---------------------------------|
| COD, mg of O/dm³          | 20,158       | 18,754       | 2,084                                           | 2,706                           |
| Alkalinity, mg-eq/dm³     | 2,200        | 2,200        | 434                                             | 826                             |
| pH                        | >12          | >12          | 10.6                                            | >12                             |

As can be seen in Table 1, deposition of sulfide ions by Ni(II) ions leads to achieving the highest degree of SAWW purification by both the COD value (89.7 %) and alkalinity (80.3 %), as compared to the results of depositing sulfide ions with Cu²⁺-containing SGS. In addition, using Ni²⁺-containing SGS as a precipitating reagent leads to reducing the medium pH value to 10.6, which eliminates the need for including additional stage of acidifying the resulting mixed wastewater with sulfuric acid until the optimal pH value is reached for oxidative cleaning processes [21].

Furthermore, it was of interest to study the stage of the advanced treatment of wastewater obtained through mixing SAWW and Ni²⁺-containing SGS to clean it from soluble hydrocarbons using oxidative methods and Cu²⁺- and Ni²⁺-containing SGSs.

Analysis of the obtained experimental data presented as graphic dependencies in Figures 1-4 showed that adding metal ions contained in SGS leads to a greater decrease in the COD values, as compared to the control experiment regardless of the oxidizer used. Ozonation is considerably more efficient than oxidation with ambient oxygen. Wastewater treatment with OAM within 30 minutes when adding 300 mg/dm³ of Cu (II) and Ni (II) ions resulted in obtaining the lowest COD values of 1,426 and 798 mg of O/dm³, respectively.

![Figure 1. Dependence of changes in the COD values of mixed wastewater on the ambient air sparging time with adding different concentrations of Ni(II) ions.](image)

Catalyst action mechanism in the processes of liquid phase oxidation of organic components is that metal ions work to transport electrons from the primary hydroperoxide oxidation product (PHOP) onto oxygen, alternately restored by RHOP and oxidized by oxygen, which leads to forming active hydroxyl and hydroperoxide radicals, intensifying oxidation processes [22-24].
At the same time, the highest purification degree of the WW mixture of 96%, is achieved by the OAM treatment with adding 300 mg/dm$^3$ of Ni$^{2+}$-containing SGS, which indicates a greater efficiency of using Ni (II) ions, as compared to Cu (II) ions.

This fact is also confirmed by the results of a series of experiments in the first SAWW treatment version presented in works [17, 19].

Given that the lowest COD value was observed in performing the oxidation process of Ni (II) components of OAM with adding Ni (II) ions contained in the SGS, a study was subsequently conducted aimed at identifying the concentrations of Ni (II) ions leading to the highest SAWW purification degree. Results of oxidizing pollutants by OAM with adding different concentrations of Ni(II) ions are shown in Figure 5.
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Figure 5 shows that, when oxidizing the pollutants by OAM within 30 minutes and adding different concentrations of Ni(II) ions, it was the concentration of 300 mg/dm$^3$, in which the lowest COD value of 798 mg of O/dm$^3$ was reached, which is lower than the requirements (1,500 mg of O/dm$^3$) for feeding to the enterprise’s leading sewerage collector that directs wastewater to the BTP.

Thus, the complex method proposed for cleaning SAWW from sulfide ions using Ni$^{2+}$-containing SGSes and soluble hydrocarbons through OAM oxidation with adding 300 mg/dm$^3$ of Ni (II) ions contained by SGS allowed us to practically completely clean wastewater from sulfide ions and reach 96% of the purification degree in terms of the COD value at the 30-minute OAM treatment. Water purified by the above method can be directed to the biological treatment facilities of an enterprise.

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