

Sewage treatment from heavy metal ions by the method of deposition, using sulfur-alkaline wastewater as a reagent

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Abstract

Aim: Wastewater, containing heavy metal ions (HMI), is formed at the metal mining, working, and manufacturing enterprises. If wastewater is not effectively treated, these contaminants enter the environment, accumulate in animals and plants, and enter the human food chain, leading to disturbances in the normal functioning of their systems and the occurrence of various chronic diseases. In this regard, wastewater treatment from HMI is an urgent task. **Materials and Methods:** This paper presents the research on purification of electroplating wastewater (EPWW) with sulfur-alkaline wastewater (SAWW), containing sodium sulfide, which is a reagent for the removal of HMI by the method of precipitation. **Result and Discussion:** It was found, that when mixing of EPWW and SAWW, dark brown sludge was formed immediately. The performed X-ray structural analysis of sludge allowed to establish, that crystals of chalcopyrite (CuFeS_2) (46%), aluminum tri-nickel (AlNi_3) (28%), and copper (II) oxide (26%) were present in its composition. Investigation of the mass of the formed sludge from the ratio of volumes of mixed EPWW and SAWW allowed to determine experimentally their optimum volume ratio, equal to 50:1, respectively. Investigation of the kinetics of sedimentation showed the possibility of applying the method of precipitation, using standard equipment for separation of sediment from the water part. It is shown, that the concentration of HMI in the treated wastewater is below the maximum permissible values of the standard indicators, established for centralized water disposal systems. Spectrophotometric method was used for the determining of iron and nickel ions in purified water; the method of stripping voltammetry was applied for revealing the ions of zinc and copper. It has been found, that when mixing wastewater, there was an increase in the values of chemical oxygen demand, which could be reduced to the discharge norms for biological waste treatment facilities ($500 \text{ mg O}_2/\text{l}$), when treating mixed water with ozone-air mixture or air oxygen for 5 and 40 min, respectively. **Conclusion:** The analysis of the results of conducted studies showed the efficiency of purification of EPWW by the method of precipitation, using as a reagent the waste product - SAWW below the established standard indices, without the use of expensive alkaline reagents and sodium sulfide.

Key words: Electroplating wastewater, heavy metal ions, ozone treatment, precipitation, sulfur-alkaline wastewater

INTRODUCTION

Ions of iron, zinc, copper, nickel, lead, cadmium, and cobalt are contained in wastewater of ore mining and processing mills, metallurgical, machine-building, metalworking, chemical, chemical-pharmaceutical, paint and varnish, textile, and other productions.^[1] Their intake with insufficiently purified sewage to the surface water bodies leads to a significant negative impact on flora and fauna of the reservoir.^[2]

The purification of wastewater from HMI is performed using the electrochemical,^[3,4]

membrane^[5,6] and sorption technologies.^[7,8] However, most of the enterprises apply the method of precipitation with the use of alkaline reagents - sodium hydroxide and calcium, - reacting with which HMI form salts, difficultly

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soluble in water. The composition and solubility of formed salts depend on the pH of the medium.^[1]

The treatment of wastewater with alkaline reagents allows to reduce the content of HMI in solution to values, comparable to the maximum permissible concentration for water bodies of cultural and social water use. However, to achieve the maximum allowable concentration limit for fishery water bodies, the treatment with alkaline reagents often does not give the necessary purification effect. In addition, a significant drawback of this method of treatment is its quality of comprising multiple stages and high cost, due to the high cost of the reagents used, as well as the need for sludge utilization.^[2]

It is known, that deeper purification from HMI is achieved in case of sewage treatment with sodium sulfide.^[1] This is due to the fact that the solubility of heavy metal sulfides is much less than the solubility of the hydroxide and carbonate compounds, traditionally used in the purification technology. At the same time, the operating range of sodium sulfide application in terms of pH is much wider than the above-mentioned compounds.^[2,9,10]

In connection with the foregoing, to increase the efficiency of wastewater treatment from HMI and to reduce its cost, the studies have been carried out on the use of sulfur-alkaline wastewater (SAWW) as a reagent, which has high alkalinity and contains significant concentrations of sodium sulfide, and therefore, is of practical interest.

METHODS

In this study, the investigations were carried out on the treatment of EPWW from HMI, applying the precipitation method, with the use of SAWW as a reagent.

At the initial stage, 850 cm³ of SAWW was placed in a separatory funnel with a capacity of 1 dm³ and was allowed to stand for 1 h, to preliminary treatment of reagent. There was the stratification into hydrocarbon (upper) and aqueous (lower) parts. Water park was drained off to the boundary surface. The value of chemical oxygen demand (COD) was determined by the accelerated method and the free alkalinity of the water part of SAWW. Then, 800 cm³ of SAWW was poured into a flask with a capacity of 1 dm³ and was subjected to simple distillation, until 6.5 cm³ of distillate was recovered (the optimal volume, experimentally established on the basis of previous studies). The bottoms liquid, cooled to 23–25°C,

was placed in a separatory funnel with a capacity of 1 dm³ and was allowed to stand for 1 h. There was the stratification into hydrocarbon (upper), aqueous (middle), and resinous (lower) parts. The aqueous part was separated from the hydrocarbon and resinous parts. The value of COD was determined by the accelerated method and the free alkalinity of the water part of SAWW. The results are shown in Table 1.

To carry out the experiment for the joint treatment of EPWW and SAWW, 250 cm³ of wastewater from galvanic production was filtered through one layer of filter paper (blank test) to separate the mechanical impurities, contained in it. The filter paper with the precipitate was dried to a constant weight at a temperature of 105°C. The filtered EPWW in the volume of 250 cm³ was poured into conical flasks with a capacity of 500 cm³. Respectively 1, 2, 3, ..., 13 cm³ of SAWW were added to each flask after preliminary settling. They were stirred for 2 min. The mixed wastewater was poured into measuring cylinders with a capacity of 250 cm³, and the kinetics of sedimentation was determined. The sludge was filtered after 24 h of precipitation, through one layer of filter paper. The filter paper with the precipitate was dried to a constant weight at a temperature of 105°C. The filtrate was used to determine the pH, COD by the accelerated method, total acidity (free alkalinity).

Spectrophotometric method was used for the determining of iron and nickel ions in purified water; the method of stripping voltammetry was applied for revealing the ions of zinc and copper.

For the purpose of post-treatment of EPWW in terms of COD, the oxidation of wastewater components with air oxygen and ozone-air mixture (OAM), with ozone concentration of 3 mg/dm³, was carried out. In the process of oxidation 100 cm³ of wastewater was poured into the oxidation reactor, and was bubbled with an oxidizer at a flow rate of 80 dm³/h during 60 min. Samples were taken in a volume of 3.5 cm³ after 5, 10, 20, 30, and 60 min of bubbling, in which the COD values were determined by the accelerated method. The sample after 60 min of bubbling was used for determining pH and free alkalinity.

RESULTS AND DISCUSSION

At the initial stage of this work, it has been established, that when mixing EPWW and SAWW, dark brown sludge is formed immediately.

Table 1: The initial and pre-treated SAWW

Type of SAWW	COD, mg O ₂ /dm ³	Free alkalinity, mg-eq/dm ³
Initial SAWW	70040	2072
SAWW after sedimentation	46512	2072
SAWW after sedimentation-distillation-sedimentation	41200	2081

SAWW: Sulfur-alkaline wastewater, COD: Chemical oxygen demand

The study of the sludge mass, obtained as a result of filtration and drying to constant weight at 105°C, from the volume of the added SAWW after preliminary settling in 250 cm³ of EPWW [Figure 1] allowed to establish experimentally, that the increase in the mass of the precipitate is observed before the addition of 5 cm³ of SAWW. Thus, it was defined the optimum volume ratio of EPWW:SAWW, equal to 50:1.

The results of the study of changes in COD, pH, acidity (alkalinity) values, when mixing EPWW and SAWW in different ratios, are presented in Figures 2-5.

From the results, presented in Figures 2 and 3, it is evident, that an increase in the volume of added SAWW in EPWW leads to an increase in COD and pH.

The most intensive increase in COD values is observed with the addition of 4 cm³ or more of SAWW, after which the dependence of COD change has a rectilinear form. That is probably due to the decrease in the amount of precipitate [Figure 1] under the created conditions and the formation of excessive sulfide ions.

The conducted studies have shown that the use of SAWW, both preliminary defecated and carried out through the sedimentation-distillation-sedimentation cycle, did not lead to a significant difference in the change of COD value and

other purification quality parameters. In connection with this, the preliminary purification of SAWW, using the cycle methods of sedimentation-distillation-sedimentation, is not advisable.

The greatest amount of precipitate is formed in the range of pH 7-10, that is connected with the possible formation along with sulfides of iron, nickel, copper, and their hydroxides.^[1]

With the addition of SAWW in amount of 3 cm³ or more, the acidity of wastewater is almost completely exhausted [Figure 4], and with a further increase in the dosages of SAWW, starting from 5 cm³, a linear dependence of the increase in alkalinity is observed [Figure 5]. That is obviously caused by the excess formation as hydroxide ions, as sodium sulfide.

The obtained kinetic curves of sedimentation of formed precipitates, and calculated on this basis the dependence of time of half lightening of wastewater from the volume of added SAWW [Figure 6] indicate that the time of lightening of most of the volume of liquid phase occurs in the first 2 h of settling.

It was found, that when adding 1 and 2 cm³ of SAWW, there was no clear interface between the sediment layer and the aqueous phase.

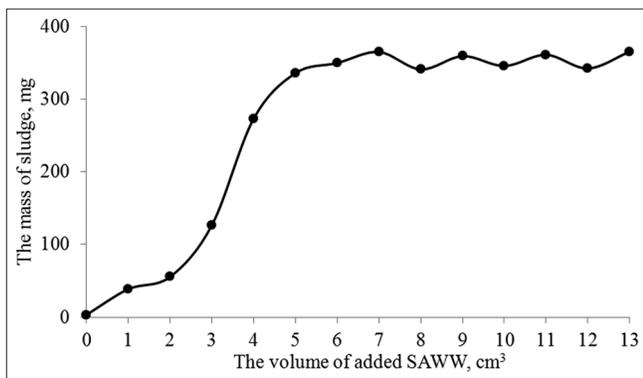


Figure 1: The dependence of the mass of sediment from the volume of added sulfur-alkaline wastewater

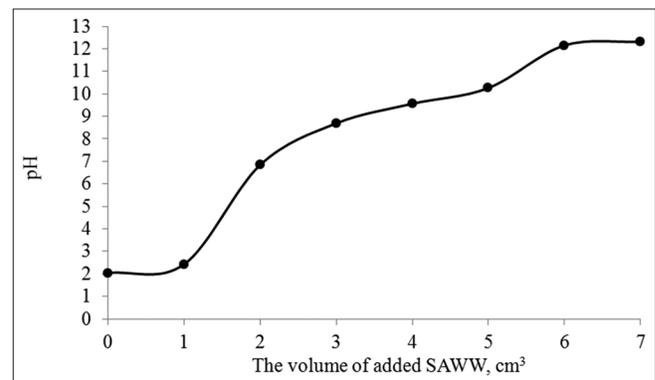


Figure 3: The dependence of the pH from the volume of added sulfur-alkaline wastewater

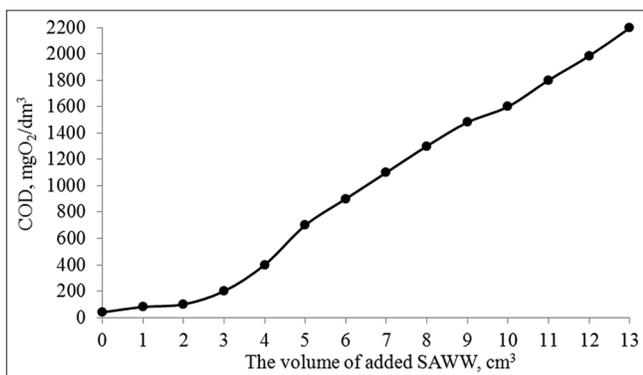


Figure 2: The dependence of the chemical oxygen demand from the volume of added sulfur-alkaline wastewater

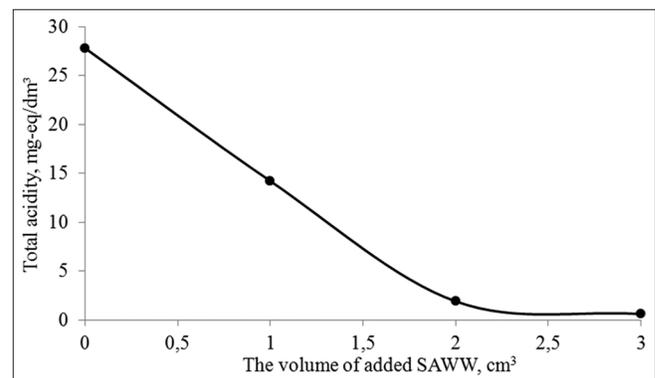
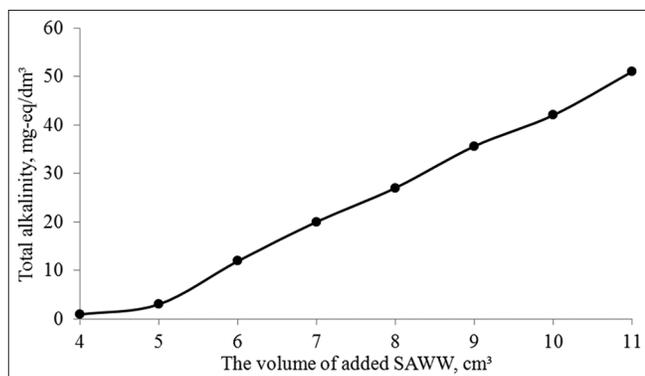


Figure 4: The dependence of the total acidity from the volume of added sulfur-alkaline wastewater

Table 2: Indicators of electroplating wastewater before and after treatment

Indicator	Before treatment	After treatment	Maximum allowable value of the indicator
Common iron ions (Fe^{2+} , Fe^{3+}), mg/dm^3	2.95	0.52	5
Nickel ions (Ni^{2+}), mg/dm^3	1.32	<0.005	0.25
Copper ions (Cu^{2+}), mg/dm^3	0.90	0.005	1
Zinc ions (Zn^{2+}), mg/dm^3	<0.001	<0.001	1
Sulfide ion (S^{2-}), mg/dm^3	-	0.02	1.5
COD, mgO_2/dm^3	39	699	500
pH	2.04	10.26	69

**Figure 5:** The dependence of the total alkalinity from the volume of added sulfur-alkaline wastewater

The analysis of the obtained data on the precipitation intensity, shown in Figure 6, confirms the correctness of the previously chosen ratio of EPWW: SAWW, equal to 50:1 (corresponding to the addition of 5 cm^3 of SAWW in 250 cm^3 of EPWW) as the optimum, since the calculated half lightening time, in the interval of addition of 5–6 cm^3 of SAWW, sharply increases from 58 to 117 min. Therefore, a further increase in the volume of SAWW to 6 cm^3 is undesirable since it will increase the required settling time.

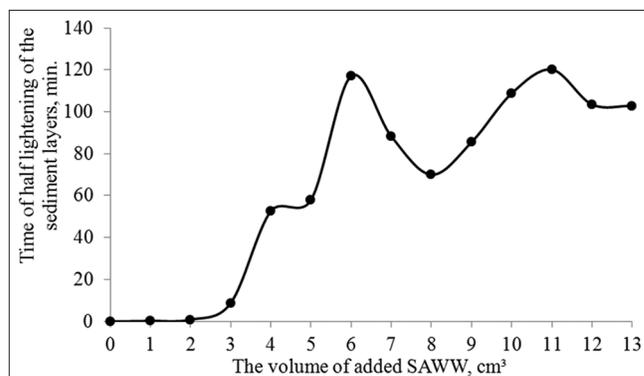
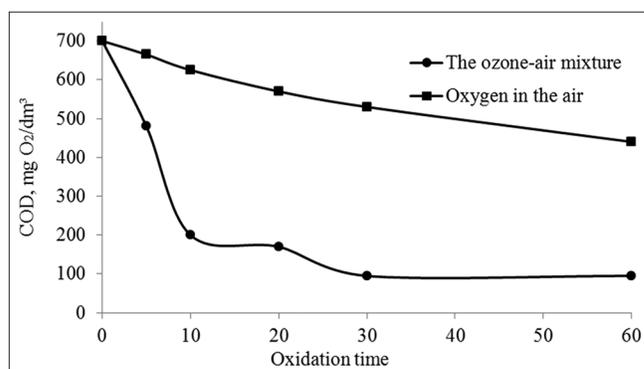
Thus, the investigation of the kinetics of sedimentation showed the possibility of applying the settling method, using standard equipment for separation of sediment, containing sulfides and hydroxides of HMI from the water part.

The obtained characteristics of the lighted part of treated EPWW, with the use of SAWW as a reagent in a volume ratio of 50:1, are, respectively, shown in Table 2.

Data, presented in Table 2, show a significant decrease of HMI in EPWW to values, lower than the maximum allowable.

To reduce the content of organic components in the mixed wastewater, further treatment by oxidation was carried out, using air oxygen and OAM as the oxidants. The results are shown in Figure 7.

Based on the data, presented in Figure 7, a decrease in COD is shown with the oxidation time, using both air oxygen and

**Figure 6:** The dependence of the time of half lightening of the sediment layers from the volume of added sulfur-alkaline wastewater**Figure 7:** The dependence of chemical oxygen demand from the time of oxidation

OAM. In this case, the process is more efficient when using ozone that is quite natural, due to its greater oxidative ability.

However, on the basis of the above norm for the considered index, equal to 500 $\text{mg O}_2/\text{dm}^3$, it is most advisable to use less efficient air oxygen as the oxidizer, which reduces COD lower than its normative content after 40 min of oxidation. That is due to its non-toxicity and significantly lower cost.

The process of wastewater components oxidizing, as by air oxygen, as by OAM, led to a decrease in pH, which after 60 min of treatment was 9.47 and 5.60, respectively.

CONCLUSIONS

The analysis of the results of conducted studies showed the efficiency of treatment of EPWW by the method of precipitation, using as a reagent the waste product - SAWW below the established standard indices, followed by oxidation of mixed wastes with air oxygen.

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