Studying the extraction of heavy-metal ions from galvanic wastewater by reagent method

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Abstract. This paper presents the study of the possibility to increase the extraction degree of heavy metal ions (HMIs) from two types of galvanic wastewater (GWW 1 and GWW 2) by the reagent method. It is established that, as a result of interaction between GWW 1 components and Na2S pentahydrate, the largest amounts of the resultant precipitate were registered in alkaline medium, which is 13.4% and 91.5% greater than in neutral and acidic media, respectively. A greater precipitate weight increase was observed when using 0.7% of Na2S pentahydrate in alkaline medium than when using 0.14% of that solution. The following efficient conditions are determined for removing HMIs from GWW 1 by the reagent method: Na2S pentahydrate solution concentration of 0.7%; volumetric reagent/GWW ratio: 1:42; alkaline medium; and retention time of 20 minutes. Implementing the method proposed allows achieving the extraction degree of 99.97% for Cu2+ ions and 99.93% for Ni2+ ions. A greater efficiency of extracting HMIs from GWW 2 was identified with adding Na2CO3, as compared to Ca(OH)2, when depositing for 25 minutes. Implementing the technique proposed for cleaning of GWW 1, GWW 2 from HMIs leads to achieving the standards of threshold limit values for fishery water bodies.

Enterprises performing chemical and electrochemical processing of metals are characterized by consuming large amounts of water necessary for implementing various process flows. Wastewater (WW) generated in such enterprises is hazardous to the environment and is the main source of HMIs entering water bodies [1].

Currently, galvanic wastewater (GWW) treatment is a pressing issue. Every year, as a result of electrochemical or chemical WW treatment processes when washing their products, enterprises bring at least 2.400 t of nickel, 460 t of copper, 3.300 t of zinc, 135 t of cadmium, and 500 t of chrome to natural water bodies [2].

Despite quite many advanced home-grown and international environmental developments, it is still essential to find an efficient and inexpensive technique of cleaning wastewater from HMIs [3, 4].

The following treatment methods are used to extract HMIs from GWW: Reagent, ion exchange, sorption, membrane, electrochemical, biological, etc. [5-21]. However, these methods are characterized by high cost, complexity in use, and generation of hard-to-recycle wastes [1, 6, 10, 12-20].

In the practice of cleaning WW from HMIs, reagent method is used most frequently, which consists in transforming metal ions into hardly soluble compounds, followed by depositing and
filtering them. Hydroxides, bicarbonates, and sulfide- and phosphate-containing materials are used as precipitators [9, 12, 13].

Benefits of reagent methods: Ease of use, versatility, wide range of initial HMI concentrations, and no need for separating wash waters and concentrates [6, 11, 12, 16].

Disadvantage of the most widely used method of cleaning WW from HMI using metal hydroxides is the impossibility of achieving the maximum permissible concentration for fishery water bodies, necessity to maintain chemical storage areas, forming galvanic sludge, and secondary water pollution [5-9, 11, 12].

Findings of the authors of works [21, 22] have shown the promising outlook of using sulfide-containing reagents in extracting HMIs from GWW. Research performed by the authors of work [23] showed the possibility of cleaning GWW from HMIs using chemical and petrochemical wastewater containing sodium sulfides, hydroxides and carbonates as precipitating reagents. Resulting from mixing such wastewater in the optimal proportions obtained, a high HMI extraction degree was detected as a suspension that easily separates from the water component. However, along with inorganic salts, sulfide-containing wastewater also contains toxic hydrocarbons, the introduction of which into GWW leads to significantly increasing chemical oxygen demand value.

On this basis, this study is aimed at finding conditions, in which a more complete HMI extraction from GWW by the reagent method would be observed, using sodium sulfide and carbonate as reagents.

Research object is GWW resulting from washing industrial products. Table 1 shows the characteristics of the GWW under research to identify efficient reagent cleaning conditions using sodium sulfide and carbonate - GWW 1 and GWW 2, respectively.

Table 1. Indicators of the GWW under study.

| Indicators                     | GWW 1 | GWW 2 |
|-------------------------------|-------|-------|
| Nickel (Ni^{2+}) ions, mg/dm³| 1.32  | 0.005 |
| Copper (Cu^{2+}) ions, mg/dm³ | 0.90  | 2.45  |
| Iron (Fe^{2+} and Fe^{3+}) ions, mg/dm³ | -     | 8.29  |
| pH value                      | 2.04  | 2.07  |

In studying the sodium sulfide use, 5 samples of GWW 1 were taken followed by adjusting the pH value. pH value of WW was adjusted using 1 N of sodium hydroxide solution. A solution of sodium sulfide pentahydrate with the concentrations of 0.14%, 0.7%, and 7% was used as a reagent to extract HMIs from GWW 1.

In studying liming processes to simulate the existing treatment procedures, 10 cm³ of 2.29% calcium hydroxide solution were added to 2 dm³ of GWW 2 (until pH = 9.07). Upon performing the liming stage and separating the sediment formed, 10 cm³ of saturated sodium carbonate solution were added to the purified GWW 2.

Figure 1 and 2 show the activities aimed at studying mass forming of precipitates in GWW 1 under research with various pH values characterizing the completeness of HMI extraction from the WW under research.

As can be seen in the histogram shown in Figure 1, the largest precipitation was observed in the alkaline medium, which indicates a more complete HMI extraction from GWW 1 studied. Neutral and acidic media show lower precipitation mass forming than the alkaline medium by 13.41 % and 91.46 %, respectively.

A greater precipitate weight increase was observed when using 0.7 % of sodium sulfide pentahydrate in alkaline medium than when using 0.14 % of the solution of the reagent used.
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Figure 1. Precipitate weight increase: I – pH=10.77, reagent used – 0.14% solution of Na$_2$S$_5$H$_2$O; II – pH=2.04, reagent used – 7% solution of Na$_2$S$_5$H$_2$O; III – pH=2.04, reagent used – 0.7% solution of Na$_2$S$_5$H$_2$O; IV – pH=10.34, reagent used – 0.7% solution of Na$_2$S$_5$H$_2$O; V – pH=7.46, reagent used – 0.7% solution of Na$_2$S$_5$H$_2$O

This is because no visual precipitate formation was observed when using the 0.14% sodium sulfide solution; however, in this case, its formation can be justified by adjusting the pH value with 1 N sodium hydroxide solution, adding of which resulted in forming large flake-shaped greenish-blue precipitates.

It should be noted that when adjusting pH values in both neutral and alkaline media, forming the flake-shaped greenish-blue precipitates was observed; however, when adding 0.7% of sodium sulfide solution to the samples under study, forming a brown precipitate was recorded in the time following. This can be explained by the fact that there was a competing reaction: When sodium sulfide solution was added, the free metal ions were bonded to sulfides producing the relevant metal sulfides, since sulfides have a lower solubility product than hydroxides [24]. Further studies were performed using 0.7% sodium sulfide pentahydrate solution, since no precipitate was observed when using sodium sulfide solution with a concentration of 0.14%, while with that of 7% there were difficulties with dosing.

Study results presented as graphic dependencies in Figure 2 showed that the most intense precipitation is observed within neutral and alkaline media. From literary reports [11, 12] it is known that with the pH value increase, the precipitation also increases; in this regard, we can argue that the results obtained are relevant to the theoretical aspect.

To study the depositing rate of the precipitate formed, we built the dependencies of the holding time upon the water volume occupied by the precipitate in neutral and alkaline media. The dependencies obtained are shown in Figure 3.

Comparing the graphic sedimentation dependencies shown in Figure 3, we can conclude that the precipitate formed in a neutral medium within the first 20 minutes was deposited faster than in an alkaline medium. The above can be explained by the fact that forming larger flakes was being observed in the neutral medium within the said time interval. Time, within which a half of the precipitate was deposited, is almost half as much in the neutral medium.

However, since this study was focused on investigating as complete HMI extraction from GWW 1 as possible, alkaline medium is the most efficient medium for depositing hardly soluble heavy metals.
In this paper, the volumetric reagent / wastewater ratio of 1:42 was found experimentally by dosing the reagent to GWW 1 under study, at which ratio the best HMI extraction efficiency is achieved. At the concentration determined and at the above volumetric ratio, we observed forming the precipitate representing large orange-brown flakes. Precipitation was brown throughout the entire volume of liquid. With the flakes increasing and thickening, the precipitate became darker, while white coating was visually identified on its surface. Then, while being dried, the precipitate changed its color from orange-brown to dark green with white impregnations. Precipitate obtained in our study was submitted for X-ray diffraction analysis. The analysis showed that the precipitate was a mixture of two compounds: Trinickel disulfide (Ni$_3$S$_2$) and copper aluminide (CuAl$_2$, an intermetallic compound) [25] in a mass ratio of 1:1.

From literary reports [26], it is known that the precipitate formed as trinickel disulfide can be used as a catalyst or for producing metal nickel.

Residual HMI content values in GWW 1 under study are shown in Table 2.

Analysis of the above tabular data showed that the concentrations of nickel and copper ions are lower than the required TLV values for fishery water, but the pH value is not included in the required range of values, which requires adjustment.

At the next stage, we studied the efficiency of extracting HMIs from GWW 2 using liming processes and a saturated sodium carbonate solution. In the first case, we observed forming suspended yellow-white substances as large flakes. After 20-minute deposition, we observed a precipitate layer that was filtered thereafter. To perform the advanced treatment of GWW 2 to clean it from HMIs, the saturated sodium carbonate was added to the treated sample, which resulted in observing the formation of suspended white substances that, upon 20 minutes of depositing, formed a denser precipitate than that obtained from using Ca(OH)$_2$, which is particularly illustrative of the better sedimentation properties of the reagent proposed and, generally, of the advanced treatment running as HMI deposition.

Values of the residual HMI contents in the GWW 2 studied are shown in Table 3.

Findings presented in Table 3 show the best efficiency in extracting HMIs from GWW 2 using sodium carbonate solution. This is because adding sodium carbonate leads to forming the least water-soluble compounds, as compared to using calcium hydroxide.

Outcomes of this study have shown that the following conditions must be observed to ensure a more complete extraction of HMIs from GWW 1: Alkaline WW medium; 0.7 % solution of sodium sulfide pentahydrate, and its volumetric ratio to GWW as 1:42, respectively.
Table 2. Indicators of GWW 1 under study upon depositing HMIs in an alkaline medium.

| Indicators | Before mixing the reagent with WW | After mixing the reagent with WW | Limit\textsuperscript{a} | Limit\textsuperscript{b} |
|------------|----------------------------------|----------------------------------|-----------------|-----------------|
| Nickel (\(\text{Ni}^{2+}\)) ions, mg/dm\(^3\) | 1.32 | 0.0009 | 0.02 | 0.01 |
| Copper (\(\text{Cu}^{2+}\)) ions, mg/dm\(^3\) | 0.90 | 0.0003 | 1.0 | 0.001 |
| pH | 2.04 | 9.83 | 6.5-8.5 | 6.0-9.0 |

\textsuperscript{a}TLV standards are approved by Order No. 78 of the Ministry of Health of the Russian Federation dated April 30, 2003 (rev. as of July 13, 2017) in accordance with the Federal Law No. 52-FZ “On Sanitary and Epidemiological Welfare of the Population” dated March 30, 1999 (Art. 1650 of the Collection No. 14 of the Legislation of the Russian Federation, 1999) and the Regulations on State Sanitary and Epidemiological Standards, approved by Decree No. 554 of the Government of the Russian Federation dated July 24, 2000 (Art. 3295 of the Collection No. 31 of Legislation of the Russian Federation, 2000).

\textsuperscript{b}TLV standards are approved by Order No. 552 of the Ministry of Agriculture of the Russian Federation dated December 13, 2016 in accordance with para. 1 of Decree No. 484 of the Government of the Russian Federation "On Procedures of Developing and Approving the Water Quality Standards of Fishery Water Bodies, Including Threshold Limit Values for the Concentrations of Harmful Substances in Water of Fishery Water Bodies" dated June 28, 2008.

Table 3. Indicators of GWW 2 under study upon depositing HMIs in an alkaline medium.

| Indicators | Before mixing the reagent with WW | After mixing Ca\((\text{ON})_2\) with WW | After mixing Na\(_2\text{CO}_3\) with WW | Limit\textsuperscript{a} | Limit\textsuperscript{b} |
|------------|----------------------------------|--------------------------------------|--------------------------------------|-----------------|-----------------|
| Nickel (\(\text{Ni}^{2+}\)) ions, mg/dm\(^3\) | 0.005 | < 0.005 | < 0.005 | 0.02 | 0.01 |
| Copper (\(\text{Cu}^{2+}\)) ions, mg/dm\(^3\) | 2.45 | 0.256 | < 0.06 | 1.0 | 0.001 |
| Iron (\(\text{Fe}^{2+}\) and \(\text{Fe}^{3+}\)) ions, mg/dm\(^3\) | 8.29 | 0.487 | 0.340 | 0.3 | 0.1 |
| pH | 2.07 | 9.07 | 10.93 | 6.5-8.5 | 6.0-9.0 |

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Subject to the conditions above, it is possible to achieve the extraction degree of 99.97% for \(\text{Cu}^{2+}\) and 99.93% for \(\text{Ni}^{2+}\). It is found that the retention of the wastewater under study for 20 minutes contributes to a more complete removal of the sediment formed resulting from the HMI deposition, which in turn proves the reasonability of using standard equipment, i.e., sump tanks.

Moreover, we have experimentally found the best efficiency of extracting HMIs from GWW 2 when using sodium carbonate as reagent, unlike calcium hydroxide, at the optimal depositing time of 25 minutes.
References

[1] Mitrakova T N 2017 Thesis of Cand. of Sci. in Engineering National University of Oil and Gas «Gubkin University», Kursk p 126

[2] Shubina A G, Sinyutina S E and Shubin R A 2009 Bulletin of TSTU 4 598-603

[3] Aleksandrov A A, Devisilov V A, Sharai E Y, Kiselyova D A et al 2018 Herald of the Bauman Moscow State Techn. Univ., Nat. Sci. 77 23-38

[4] Aleksandrov A A, Devisilov V A and Sharai E Y 2020 Herald of the Bauman Moscow State Techn. Univ., Nat. Sci. 88 32-45

[5] Shaikhiev I G, Zhelnovach O G, Zaripov R M and Zubrilova N V 2008 Ecology and Industry of Russia 6 14-5

[6] Vinogradov S S 1998 Environmentally friendly galvanic production (Moscow: Globus) 302 p

[7] Perelygin Yu P, Zorkina O V, Rashevskaya I V and Nikolaeva S N 2013 Reagent wastewater treatment and disposal of waste solutions and sediments of galvanic industries (Penza: PSU) p 80

[8] Gorban I Yu 2015 Aspirant 5-1 34-6

[9] Ershova A Yu 2016 Aspirant 1 16-7

[10] Makisha N and Yunchina M 2017 MATEC Web of Conferences 106 1-6

[11] Andreev S Yu, Demidochkin V V, Kochergin A S et al 2010 Regional architecture and construction 1 107-11

[12] Shtripling L O and Turenko F P 2005 Basics of wastewater treatment and solid waste recycling (Omsk: OmGTU) p 192

[13] Zhdanova A V and Ilarionova S A 2012 Bulletin of Perm University 1 54-60

[14] Karmanov V V and Karandashova O E 2010 Scientific Research and Innovation 4 64-6

[15] Gunatilake S K 2015 Journal of Multidisciplinary Engineering Science Studies 14 14-8

[16] Zilberman M V, Nalimova E G and Tingaeva E A patent RF 2125972, IPC C02F1/62 C02F1/58 Method for waste water purification from heavy metal ions. Published on 10.02.1999

[17] Pimneva L A 2013 Modern knowledge-intensive technologies 2 99-101

[18] Dukhin S S, Sidorov M P and Yaroshchuk A E 1991 Electrochemistry of membranes and reverse osmosis (Leningrad: Khimiya) p 192

[19] Ilyin C I 2013 Electromembrane processes (Moscow: Mendeleev Univ. of Chem. Eng.) p 57

[20] Dolina L F 2008 Advanced Technology and Process Machinery for Cleaning of Wastewater from Heavy Metal Salts (Dnepropetrovsk: Continent) p 254

[21] Borbat V F, Mukhin V A, Adeeva L N, Novikova I M and Sharkova G I patent RF 2033972, IPC C02F1/62 Method for treating waste water from electroplating production from heavy metal ions. Published on 30.04.1995

[22] Kondratyev A S, Smakov M R and Dekhtyar E F patent RF 2572327, IPC C02F1/58, C02F1/62, CO1G3/12, CO2F101/20, CO2F103/36 Method for treating copper-containing wastewater from acrylic acid production (options). Published on 20.11.2015

[23] Fazullin D D, Mavrin G V, Savelyeva A V, Savelyev S N, Dryakhlov V O and Shaikhiev I G 2017 International Journal of Green Pharmacy 10-12 831-5

[24] Rabinovich V A and Khavin Z Ya 1978 Brief Reference on Chemistry (Leningrad: Khimiya) p 392

[25] Shiroky G T, Bortnitskaya M G and Yukhnevsky P I 2012 Materials Science for Installers of Process Equipment, Pipelines, and Steel Structures (Minsk: Vysshaya shkola) p 301

[26] Trinickel disulfide. Chemistry and toxicology. Electronic resource: http://chemist.ru/Database/properties.php?dbid=1&id=9561