

PROFESSIONAL PAPER

Procedures of chemical wastewater purification of galvanic chemical processes and quality of purified water

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Abstract

The procedures of chemical purification of wastewater with chemical changes of polluting water substances are: neutralization – adjusting the pH value by adding acids or bases; flocculation – joining of dissolved particles into larger flakes that settle; coagulation – addition of chemical substances for faster precipitation; ion exchange – the process of ion exchange between solids (ion exchangers) and liquids (electrolyte solution); and oxidation – removal of various substances from wastewater by oxidants (chlorine, chlorine dioxide, ozone, hydrogen peroxide, etc.). Technological processes of galvanic-chemical protection, according to qualitative-quantitative characteristics, represent one of the most complex pollutants of wastewater. In the processes of galvanic-chemical protection in “Orao” a.d. Bijeljina, according to the nature of its origin, wastewater contains: free acids and bases; specific contaminants: cyanides, chromates, and nitrates; and dissolved heavy metals: Fe, Cd, Ni, Cu, Zn, Ag and others. Applying the shown (and other) procedures, as well as their suitable combination, in the wastewater treatment plant, the quality of purified water is obtained, which, according to the legislation in the Republic of Srpska, can be discharged both into the river recipient and into the public sewage system. The paper presents some of the segments of complex chemical procedures for the treatment of polluted wastewater, while the obtained results of testing of treated industrial wastewater refer to the sample for the II quarter of 2024.

Keywords: electroplating, procedures, waste water, quality

1. INTRODUCTION

In the procedures of galvanic chemical protection in “Orao” a.d. Bijeljina (seven installed lines), in addition to basic industrial solutions, there is also a significant number of auxiliary (interphase) industrial solutions. The application of metal coatings is most often carried out in acidic electrolytes, the composition of which is of essential importance from the aspect of the composition of wastewater, because after the application of metal coatings, mandatory rinsing is performed (Arsenović 2012). The basis of acid electrolytes is the hydrated salt of the metal that is applied, and to increase the conductivity of the electrolyte, acids are used, namely sulfuric acid for copper and chromium, and boric acid for nickel and cadmium. The composition of these electrolytes includes surfactants that improve the quality of the finished product.

The application of metal coatings requires successive immersion of the object in several solutions where processes of a chemical and electrochemical nature are carried out. Due to their geometric shape and the phenomenon of adhesion, when coming out of any solution, the objects drag with them a quantity of liquid that cannot be ignored. That is why the items must be thoroughly rinsed before proceeding to the next stage of processing. This washing causes the creation of wastewater containing: free acids and bases; specific contaminants: cyanides, chromates and nitrates; and dissolved heavy metals: Fe, Cd, Ni, Cu, Zn, Ag and others (Arsenović 2012; Stjepanović 2013a). Table 1 shows the installed metal surface protection lines and the nature of wastewater generated in individual processes.

Table 1. Lines of surface protection and character of wastewater.

Line	Procedures	Industrial solutions on lines of galvanic-chemical procedures	Wastewater characteristics
1	Anodizing and chromatography	NaOH; sav.rin. ¹⁾ ; rin.w.dwat ²⁾ ; sav.rin; HNO ₃ ; Anodic ox. in H ₂ SO ₄ ; Anodic ox. in CrO ₃ ; sav.rin.; K ₂ Cr ₂ O ₇ ; force in H ₂ O; Preparation of Mg; sav.rin; rin.w.dwat; Chromatization of Mg; Chromatization of Al.	Alkaline and acid; Sour; Lame
2	Zinc plating and cadmium plating	El.deg. ³⁾ ; sav.rin; rin.w.dwat; sav.rin; HCl; Acid chloride Zn; (rin.w.dwat); Passivizations: blue; (etc.); Cd; SMB (rin.w.dwat) and black passivation. ^{1)saving rinsing; 2)rinsing with demi water; 3)electrochemical degreasing.}	Alkaline and acid; Sour; Alkaline; Lame; Cyanide
3	Nickel plating	El.deg.; sav.rin; rin.w.dwat; sav.rin; H ₂ SO ₄ ; Movie Ni; Nickel plating (Watts type); sav.rin; rin.w.dwat.	Alkaline and acid; Sour
4	Hard chrome plating	sav.rin; rin.w.dwat; Hard chrome plating; Chrome sulfuric acid; Download Cr; rin.w.dwat.	Lame; Sour
5	Silver plating and copper plating	El.deg.; sav.rin; rin.w.dwat; sav.rin; HCl; Film Ag; Silvering; sav.rin.; rin.w.dwat; Na ₂ Cr ₂ O ₇ ; rin.w.dwat; Cyanide copper plating; sav.rin.; rin.w.dwat.; Downloading Ni.	Cyanide; Sour; Alkaline and acid; Lame
6	Manual line for different procedures	NaOH; rin.w.dwat; Galvanizing; rin.w.dwat; KCN; HNO ₃ ; HNO ₃ -passivation; rin.w.dwat; Ni-sulphamate nickel plating; sav.rin.; rin.w.dwat.	Cyanide; Sour; Alkaline; Lame
7	Burnishing and phosphating	El.deg.; sav.rin; rin.w.dwat.; sav.rin.; H ₂ SO ₄ ; Phosphating; sav.rin.; rin.w.dwat.; Browning; sav.rin.; rin.w.dwat.; Browning; KMnO ₄ ; sav.rin.; rin.w.dwat.	Sour; Alkaline; NO ₂ /Alkaline

The paper presents some of the segments of complex chemical procedures for the treatment of polluted wastewater (Arsenović 2024), their chemistry, as well as the obtained results of testing the quality of purified wastewater for the second quarter of 2024.

2. EXPERIMENTAL PART

The wastewater treatment plant from surface protection lines (Table 1) consists of:

- Ion exchangers for CN⁻ rinse water (silvering and copper plating lines; cadmiumizing; manual line for different processes), Figure 1a;
- Ion exchangers for rinsing water without CN⁻ (anodizing and chrome plating lines; zinc plating; nickel plating; burnishing and phosphating), Figure 1b;
- Concentrate and rinse water tanks;
- Reservoir for batch treatment of wastewater;
- Sludge filtering;
- Selective cleaning of the filtrate with Cd;
- Selective cleaning of filtrate without Cd;
- Final neutralization; and
- Final control of pH values (Plaming Skupina 2012).

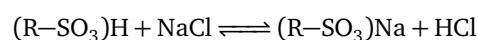
3. RESULTS AND DISCUSSION

Constituent parts of the wastewater treatment plant are the control cabinet and a computer with a user program for working on the automated lines of surface protection, treatment of wastewater and polluted air, which

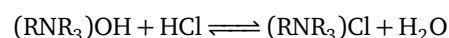
is drained from the surface of industrial solutions to the plant for its purification – wet purification procedures.

After the galvanic procedures, the rinse water (after rinsing with demi H₂O) from the rinse tank reaches the circular water tank by free fall, from where it is transferred through the cartridge filter to the columns with ion exchangers (Stjepanović 2013b).

In the cation exchanger, the cations present in the water are replaced with H⁺ ions, whereby, as a result of this exchange, free acids are formed that correspond to the salt content in the rinse water:



In the anion exchanger, anions are replaced with OH⁻ ions:



Purified water at the outlet from the ion exchangers corresponds in quality to distilled water and, as such, is returned to the rinsing tanks. When the exchangers are saturated, their regeneration is carried out: cation exchangers with HCl and anion exchangers with NaOH.

Waste concentrates from the line and ion exchange regenerates are collected in concentrate tanks. Due to the wide variety of processing procedures, concentrates are collected individually: tank of acidic concentrates; basic; NO₂ concentrate tank; Ni; acidic Cd concentrates; Cr; CN concentrate tank; and CN concentrate tank Cd.

From the tank, the concentrates are transferred to the batch processing tank, where, based on the composition



(a) Cation and two anionic JI-columns¹ with pipe distribution with valves, injectors, H₂O flow meters and regeneration agents, pressure gauge, conductometer and cartridge filter on the support structure for CN⁻-washed water.

¹In the three JI-columns there are strongly acidic, weakly basic and strongly basic resin (Stjepanović 2013a).



(b) Cation and anion JI-columns² with pipe distribution with valves, injectors, H₂O flow meters and regeneration agents, pressure gauge, conductometer and cartridge filter on the support structure for rinse water without CN⁻.

²In the two JI-columns there is a highly acidic and weakly basic resin (Arsenović 2024; Stjepanović 2013a)

Figure 1. Ion exchange columns in the wastewater treatment plant.



(a) Concentrate batch processing tank.

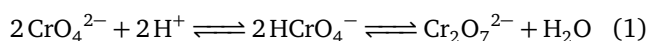


(b) NaOCl and NaOH dosing container.

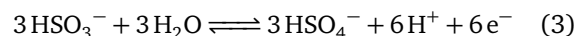
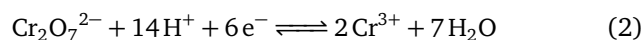
Figure 2. Batch processing equipment.

of the concentrate, they are processed: chromate reduction (Cr⁶⁺ to Cr³⁺), nitrate oxidation, cyanide oxidation and neutralization and precipitation of heavy metals, Figure 2a.

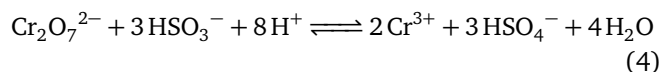
Reduction of chromate (Cr⁶⁺ to Cr³⁺). Chromic wastewater contains Cr⁶⁺ in the form of chromate (CrO₄²⁻) in the neutral and alkaline pH region, and in the form of dichromate (Cr₂O₇²⁻) in the acidic region. Chromate in the acidic region changes, through the transitional form of hydrochromate, into dichromate and water:



Reduction of Cr⁶⁺ is achieved by the addition of a suitable reducing agent, sodium bisulfite (NaHSO₃):

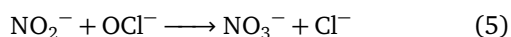


Adding equations (2) and (3) gives:



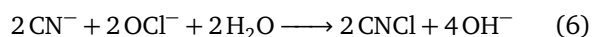
The time required for the reaction is 15–20 minutes.

Oxidation of nitrite (NO₂⁻ to NO₃⁻). Decontamination of NO₂⁻ is achieved with a NaOCl solution (with 13–15% active Cl):

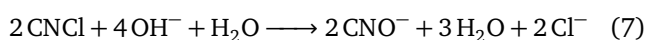


The reaction takes place at pH 3–4 for a reaction time of approximately 10 minutes.

Oxidation of cyanide (CN^-). Cyanide wastewater contains free and complexed cyanides. Decontamination of CN^- is achieved with NaOCl solution (13–18% active Cl). The reaction mechanism occurs in three stages:

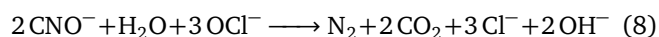


The reaction is very fast and occurs at all pH values. The resulting cyanogen chloride is very toxic, which is why it is converted to cyanate in the next stage:

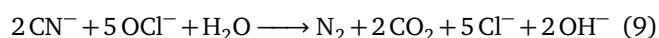


The hydrolysis reaction is slow and exothermic; the reaction rate depends on the pH value and is fastest at pH 10.5–12. The required pH value is achieved by adding NaOH or $\text{Ca}(\text{OH})_2$. The time required for stages I and II is 40–60 minutes.

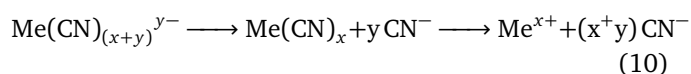
In the third stage, cyanate is converted to N_2 and CO_2 :



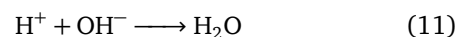
The general equation of CN^- oxidation is:



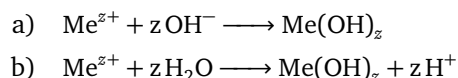
Decontamination of CN^- metal complexes is highly dependent on their dissociation ability (only dissociated CN^- participates in the reaction):



Neutralization and removal of heavy metals. Acidic and alkaline waste waters have an aggressive character. Their partial neutralization is done by mutual mixing, and complete neutralization with the addition of a neutralizing agent. In addition to free acids and bases, these wastewaters also contain heavy metal ions. Neutralization of free acids and bases proceeds according to the reaction:



In addition to neutralization, precipitation of heavy metals (Fe, Zn and Cr) is carried out in the form of metal hydroxides or metal base salts:



For the precipitation of metals above pH 7, equation (a) applies; below pH 7, equation (b). The most favorable pH value for quantitative precipitation of metals is between 7.5–9.5 with the optimum at pH 9.2. Precipitated $\text{Fe}(\text{OH})_3$ serves, at the same time, as a flocculant for other impurities. Each Me-ion has a specific pH value at which it is best excreted as MeOH and precipitates in the form of sludge. Thus, Fe(III) precipitates already in the acidic region, Cr(III) at pH < 8, Zn(II) at pH > 8.5 and Ni at pH > 9.5. The optimal pH value is 9.2. The reaction takes place with intensive mixing.

For the analysis of wastewater in the operating laboratory, already prepared quick tests are used for the detection of certain heavy metals, as well as for the detection of cyanide, Cr^{6+} and nitrite.

After the processing is completed, the sludge is filtered on a filter press. The clear filtrate goes to the selective cleaning tank, and the created sludge is packed in filter bags and handed over to the authorized operator for further disposal. In a column with a selective exchange resin (which has a high affinity for heavy metals), the heavy metals present are exchanged with the Na^+ ion. When the resin is saturated, it needs regeneration with HCl and NaOH.

The treated water, after selective cleaning, is pumped into the final neutralization tank (Figure 3a), where the pH value is corrected before being discharged into the drain. The pH value is maintained between 7–9 and regulated with HCl and NaOH. The water from the final neutralization flows into the final pH value control (Figure 3b). In case of deviation of the pH value, an alarm is activated and the selective cleaning pump is switched off. In this way, improperly processed wastewater is prevented from flowing into the drain. After the previously described procedure of purification of wastewater from galvanic-chemical processes, water is sampled from the control shaft at the outlet of the industrial wastewater treatment plant. The analysis of purified water was carried out in a laboratory accredited by BATA, “Water Institute” Bijeljina (Water Institute Bijeljina 2024).

The analysis of purified water from the plant is performed four times a year. The results of the analysis of purified water refer to samples analyzed in 2024, Table 2.



(a) Final neutralization tank.



(b) Final pH control.

Figure 3. Final treatment stages.

Table 2. Results of the analysis of purified water in 2024.

Tested parameter	Test method	Unit	Results				Permissible limit value
			1. quarter	2. quarter	3. quarter	4. quarter	
Water temperature	Standard methods 2550-B APHA-AWWA-WEF 2023	°C	14.5	20.6	20.1	15.0	30
pH value	BAS ISO 10523:2013	–	7.30	7.26	7.18	7.25	6.5–9.0
Sedimentability	Standard methods 3111-B APHA-AWWA-WEF 2023	ml/l	< 0.5	< 0.5	< 0.5	< 0.5	0.5
HPK (O ₂ bichromate)	Standard methods 2540-F APHA-AWWA-WEF 2023	g/m ³	9.2	3.4	6.6	< 3.0	125
BPK (after 5 days)	BAS EN 1899-2:2002	g/m ³	1.27	0.82	0.60	0.81	25
Total suspended solids	BAS ISO 11923:2002	g/m ³	< 1	2.24	2.5	5.90	35
Ammonia nitrogen	BAS ISO 7150-1:2002	g/m ³	0.049	0.170	0.048	0.034	10
Nitrate nitrogen	BAS EN ISO 10304-1:2010	g/m ³	5.05	6.26	3.72	3.84	10
Nitrite nitrogen	BAS EN 26777:2000	g/m ³	< 0.001	0.02	0.001	0.002	1
Total nitrogen (Kjeldahl)	BAS EN 25663:2000	g/m ³	< 0.2	< 0.2	0.365	1.19	–
Total nitrogen	Calculated from nitrite, nitrate and Kjeldahl nitrogen	g/m ³	5.25	6.46	4.09	5.03	15
Total phosphorus	BAS ISO 6878:2006	g/m ³	0.009	0.014	0.004	0.029	3
Fluorides	BAS EN ISO 10304-1:2010	g/m ³	< 0.10	< 0.10	< 0.10	< 0.10	2
Sulfates	BAS EN ISO 10304-1:2010	g/m ³	26.84	42.79	31.07	28.97	200
Chlorides	BAS EN ISO 10304-1:2010	g/m ³	22.22	38.96	30.79	44.57	250
Iron	Standard methods 3111-B APHA-AWWA-WEF 2023	g/m ³	< 0.03	< 0.03	< 0.03	< 0.03	2
Silver	Standard methods 3113-B APHA-AWWA-WEF 2005	mg/m ³	1.32	1.25	1.27	1.62	50
Total chrome	BAS ISO 9174:2000	mg/m ³	2.45	13.0	2.68	0.870	100
Copper	Standard methods 3113-B APHA-AWWA-WEF 2023	mg/m ³	2.87	17.16	3.57	< 0.50	300
Nickel	Standard methods 3113-B APHA-AWWA-WEF 2023	mg/m ³	< 0.50	< 0.50	< 0.50	< 0.50	10
Cadmium	Standard methods 3113-B APHA-AWWA-WEF 2023	mg/m ³	< 0.05	< 0.05	< 0.05	< 0.05	10
Zinc total	BAS ISO 8288:2002	g/m ³	< 0.005	< 0.005	0.195	0.030	1
Hexavalent chromium	Standard methods 3113-B APHA-AWWA-WEF 2023	mg/m ³	1.92	4.62	< 0.05	< 0.50	100
Cyanides	Spectrophotometer PC Lovibond – Pyridine-barbituric acid, MT.NO.157	g/m ³	< 0.01	< 0.01	< 0.01	< 0.01	0.1
Sulfites	Spectrophotometer PC Lovibond, MT.NO.370	g/m ³	< 0.05	< 0.05	< 0.05	< 0.05	1

As shown in Table 2, all tested parameters in the analyzed samples of purified water meet the criteria prescribed by the Rulebook (Regulation on Conditions for Discharge of Wastewater into Surface Waters – (Official Gazette of the Republic of Srpska 2001)).

4. CONCLUSION

Applying the procedures (as well as their proper combination) of wastewater purification of galvanic-chemical processes, the quality of purified water was obtained, which, in accordance with the legal regulations in the Republic of

Srpska (Regulation on conditions for discharge of wastewater into surface waters) can be discharged into surface waters. From the environmental engineering aspect, the company "Orao" a.d. fulfils the requirements of wastewater treatment established by law.

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