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TRENDOVI U POSLOVANJU
NAUČNO-STRUČNI ČASOPIS

EFIKASNOST POGONA ZA GALVANSKO TRETIRANJE OTPADNIH VODA "FRAD" ALEKSINAC

THE EFFICIENCY OF GALVANIC WASTEWATER TREATMENT FACILITY 'FRAD' IN ALEKSINAC

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Sažetak

Tehnološki proces Galvano-hemijske zaštite, prema kvalitatino-kvantitativnim karakteristikama, predstavlja jedan od najsloženijih zagađivača otpadnih voda. Veliki broj zagađivača (metalni joni, cijanidi, kiseline, baze, masnoće i ulja, organski rastvarači, surfaktanti, fosfati, itd.), koji se nalaze u galvanskoj otpadnoj vodi se tretiraju konvencionalnim metodama (hemijska oksidacija i redukcija, neutralizacija, sedimentacija, koagulacija i flokulacija). Razlog zbog koga su sistemi za tretiranje galvanskih otpadnih voda konvencionalni u Republici Srbiji je ekonomske prirode.

Ova studija je urađena radi procene učinka Pogona za tretiranje kanalizacionih voda u Aleksincu. kompanije "Frad" u oblasti koja se zasniva na Sekvencijalnom serijskom reaktorskom procesu. Učinak ovog pogona je suštinski parametar koji treba posmatrati jer se tretirana otpadna voda ispušta u reku Moravicu. Procena učinka će takođe pomoći u boljem razumevanju dizajna i operativnih poteškoća (aeracija, kompresori, itd.) u Pogonu za tretiranje kanalizacionih voda.

Cilj istraživanja: Efikasnost pogona koji tretiraju kanalizaciju može se ilustrovati studijom o proceni nivoa zagađivača ulaznih i izlaznih voda u pogonu za tretiranje kanalizacione vode koja se ispušta u okolinu

Abstract

The technological process of Galvano-chemical protection, according to qualitatively-quantitative characteristics, represents one of the most complex contaminants in wastewater. A large number of contaminants (metal ions, cyanides, acids, bases, grease and oils, organic solvents, surfactants, phosphates, etc.), found in galvanic wastewater are treated through conventional methods (chemical oxidation and reduction, neutralization, sedimentation, coagulation and flocculation). The reason why galvanic wastewater treatment systems in the Republic of Serbia are conventional is of economic nature.

The present study has been undertaken to evaluate the performance of Sewage Treatment Plant located at Aleksinac, Company of "Frad" district which is based on Sequential Batch Reactor process. Performance of this plant is an essential parameter to be monitored as the treated effluent is discharged into the Moravica River. The Performance Evaluation will also help for the better understanding of design and operating difficulties (aeration, blowers, etc.) in Sewage Treatment Plant.

Research goal: The efficiency of sewage treatment plants can be illustrated by a study on the evaluation of pollutant levels of the influent and the effluent at the treatment plant of sewage treatment plants discharging into the environment.

Ključne reči: *otpadne vode, tretiranje galvanske vode, Galvano-hemijska zaštita*

Keywords*: wastewater, galvanic water treatment, Galvano-chemical protection*

JEL klasifikacija*: Q25*

1. Introduction

Water is one of the most important and sensitive natural resources whose quality hasn't been taken care of for a long time in Serbia and worldwide. Every environmental change caused by humans reflects directly or indirectly on water resources [1]. The preservation and control of water quality is becoming increasingly more significant considering the continual reduction of available drinking water in the world. Drinking water reserves are in surface and underground flows so continued contamination would in time certainly lead to a greater reduction of available resources considered inexhaustible until recently.

The technological process of galvano-chemical protection, according to qualitatively-quantitative characteristics represents one of the most complex wastewater contaminants [2]. This process demands a successive immersion of objects into multiple solutions where various chemical and electrochemical processes occur. Due to their geometrical shape and the phenomenon of adhesion, when exiting a solution the objects pull a quantity of liquid which cannot be ignored. Because of this, before transitioning to the next stage of processing the objects must be washed thoroughly [2, 3]. That rinsing creates wastewater containing: free acids and bases; specific contaminants: cyanide, chromates and nitrates and dissolved heavy metals: Fe, Cd, Ni, Cu, Zn, Ag, etc. [2-6]. The steps and mechanisms in the treatment of wastewater created in the process of galvano-chemical protection are shown in the research. The research represents a summary overview of the ecological aspect of the treatment of wastewater made in the process of galvano-chemical protection of metal parts as a result of adherence to the legislation of the Republic of Serbia in the area of wastewater. Galvanic wastewater significantly contributes to soil contamination, and surface and underground water contamination. These waters with a low pH value and heavy metal concentrations up to one hundred times higher than the limit values for discharge into the environment are frequently discharged into agricultural soil and the surrounding watercourses [7]. Acid wastewater upon contact with the ground, sediment, mobilize heavy metals and other toxic matter thereby causing contamination of agricultural soil and drinking water sources, as well as contamination of water for food production; that is, there is increased bioavailability and accumulation in plant and animal materials used in the production of human food. A high cytotoxic and genotoxic potential of these waters was confirmed on bacteria [8], plant test systems [9] and human cells [8-10]. So far, many methods for the treatment of this type of effluent have been developed with the view to reduce the negative impact on the working and living environment and indirectly on human health. Some of these methods are chemical oxidation and reduction, neutralization, sedimentation, coagulation and flocculation [11, 12].

The goals of this research are the selection and application of an optimal set of suitable methods for the treatment of wastewater made in the process of surface metal protection through alkaline cyanide-free galvanizing and chemical nickel plating, and also, the optimization of all operative parameters with a view of achieving effluent quality parameters that are significantly lower than the determined limit values. Also, the goal is to achieve significantly lower values than the ones that can produce a toxic effect on the most sensitive test analyses while keeping the time and energy consumption per unit of processed water to the minimum.

2. Sources of Effluent Caused by Galvano-chemical Processes

The application of metal coating is commonly performed in acid or alkaline electrolytes whose composition is crucial from the point of view of wastewater structure, because rinsing must follow the application of metal coating [13, 14]. Zinc coating is the most widespread because zinc is a cheap metal, it may be precipitated from various electrolytes and it is resistant to corrosion which is why galvanizing is continually perfected. Zinc coating is most commonly used for protection of iron and steel because in the galvanic coupling of zinc and iron, zinc plays the role of the anode and protects the core metal from corrosion. Surfactants that improve the quality of the finished product are included in the composition of these electrolytes [13]. The main advantages of alkaline cyanide-free electrolytes area remarkably low price of forming chemicals and a great coating power and a depth effect as well as subsequent malleability or swaging of processed objects. Considering this data the best characteristics of standard galvanizing electrolytes have been used and optimal quantities of iron, nickel or cobalt have been added in the form of a suitable complex compound which leads to the conditions for the deposit of zinc alloy.

Chemical nickel has an outstanding resistance to corrosion, good resistance to wear, it is evenly hard, can be subsequently welded to other objects and it has an exceptional decorative feature.

Table 1 shows the installed lines of surface metal protection and the characteristics of wastewater made in distinct steps.

Table 1. Lines of surface protection and wastewater characteristics in "Frad" Aleksinac

Line	Steps	Industrial solutions	Wastewater
1	Electrolytic degreasing	NaOH; surfactants	Alkaline
1	Cold rinsing	NaOH;	Alkaline
1	Staining and erosion of surface	HCL	Acid
1	Cold rinsing	HCL	Acid
1	Electrolytic cyanide-free galvanizing	NaOH (100 – 130 g/L), Zn (8 – 12g/L),Fe (80 – 120 mg/ L) T (15 – 35 ºC), gloss additives.	Alkaline
1	Double cold rinsing	NaOH	Alkaline
1	Blue passivation	Passivation: blue, HNO_3	Acid Chromic
1	Cold rinsing		Acid
2	Electrolytic degreasing	NaOH	Alkaline
2	Cold rinsing		Alkaline
2	Chemical nickel plating	$Na_2S_2O_3$,,$NiSO_4CH_3COOH$, lactic acid KOH, T (80 – 85 °C) pH 4-5	Acid
2	Cold rinsing		Acid

3. Neutralization and Precipitation of Heavy Metal Ions

Acid solutions are used for eroding the base metal (cleaning the surface before applying coating) and for eroding the zinc coating (removal of inadequate coating and the coating applied to suspenders). Usually hydrochloric acid solutions are used. During the erosion in the working solution the concentration of metal ions is increased whereas the concentration of the acid is reduced.

Acidic wastewater and base wastewater are aggressive. Their partial neutralization is accomplished through mixing and complete neutralization is achieved by adding a neutralizing agent. Beside the free acids and bases this wastewater also contains heavy metal ions. The neutralization of free acids and bases happens according to the following reaction:

$H^{+} + OH^{-} = H_2O$ (1)

Aside from neutralization there is also heavy metal precipitation (Fe, Zn and Cr) in the form of metal hydroxides or metal base salts.

a) $Me^{z+} + zOH^{-} = Me(OH)z$ (2)

b) $Me^{z+} + zH_2O\ Me(OH)z + zH^{+}$ (3)

Metal precipitation above pH 7 goes according to the equation (2) and below pH 7 according to the equation (3). The pH value that is the most conducive to quantitative precipitation is between 7.5 to 9.5 with the optimal value being pH 9.2. The precipitated Fe $(OH)_3$ simultaneously serves as a flocculent for other impurities. Every Me^{z+} (metal ion) has a specific pH value at which it is isolated as MeOH and precipitated as sludge. Nascent ions Al^{3+} and Fe^{2+} are very efficient coagulants and flocculants. Aluminium ions with water create a large number of network shaped compounds Al-O-Al-OH which have the ability to chemically absorb pollutants such as F- or similar. Aluminium is generally used in treating drinking water and iron in treating wastewater [15].

Reactions happen in the facility's reactor with intense mixing. After processing the sludge is filtered in filter-strainers. Clear filtrate goes to the corresponding selective cleaning tank and the formed smudge is packed into filter bags and deposited accordingly.

Rinsing wastewater is processed continuously or discontinuously in neutralization pools. Considering the composition of the degreasing solution as well as the chemical reactions happening in this solution rinsing alkaline water generally contains: sodium carbonate, sodium hydroxide, sodium phosphate, surfactants and suspended matter [21, 22]. Acid water used for rinsing, considering the composition of the eroding solution and the chemical reactions happening in the solution, contains: hydrochloric acid, iron chloride, iron oxides, iron hydroxide and elemental iron. Acid and alkaline rinsing water is collected in a common waterway, mixed and partially neutralized where the degree of neutralization depends on the ratio between the amount of water and the concentration of water. The technological processing of wastewater incorporates a removal of coarse particles, removal of grease, neutralization, precipitation and filtration of sludge. Processed water free falls into the precipitation pool. The sludge deposited in the precipitator is neutral and it contains from 2 to 6 % of dry matter.

An additional problem is that this sludge is categorized as hazardous waste due to a high content of chlorides, which prevents further use of this waste [15, 16].

4. Experimental Part

After the previously described wastewater treatment which is made in the lines of galvano-chemical protection, water is sampled from the facility's tanks where the water is accumulated before release. The analysis of this water was performed in a lab accredited by the Ministry of Health of the Republic of Serbia, "Institut za Javno Zdravlje" (Public Health Institute) in Niš. The research shows the results of the analysis from the first and the fourth quarter of the previous year and the analysis of water from this facility is performed four times a year.

5. Results and Discussion

Parameters in the research were determined before and after the treatment for galvano-chemical protection in the galvanic wastewater treatment facility and a degree of purification for each parameter was set. The results of galvanic wastewater analysis before and after the treatment in the facility for the treatment of wastewater made by galvano-chemical protection, the degree of purification, and MAC (maximum allowed concentration) values of the analyzed parameters for the first and the fourth quarters are given in table 2 and table 3.

Table 2. The results of sample analysis before and after the treatment and the assessment of the degree of purification of "Frad"Aleksinac (the first quarter)

Parameter	Examination methods	Sample 1 Wastewater before the purification device	Sample 2 Wastewater after the purification device	% the degree of purification	MAC
Sedimentary matter (mL/L/2h)	Stand. methods 5220D(APHAAWWWA-WEF) 2005.	200,0	0,0	100,00	25
pH value	BAS ISO 10523.2002	1,0	7,8		6,8-8,5
Sulphates SO_2 (mg/L)	BAS EN ISO 10304-1:2002	1060	26,5	97,41	25
Unfiltered water evaporation residue (mg/L)	BAS ISO11923:2002	16410	180	98,29	100
Filtered water evaporation residue (mg/L)	BAS ISO11923:2002	14190	74	98,07	25
Suspended matter, (mg/L)	BAS ISO11923:2002	2220	6	99,73	30
The consumption of $KMnO_4$, (mg/L)		940	19,8	97,89	20
Chlorides HCl, (mg/L)	BAS EN ISO 10304-1:2002	22400	18	99,92	25
Nitrates N, (mg/L)	BAS EN 10304-1:2002		14		10
Nitrites N, (mg/L)	BAS EN 10304-1:2002		0,005		0,05
Ammonium ion, (mg/L)	BAS EN 25663:2000	250	0,05	99,98	1
Anionic detergent. (mg/L)	Stand. methods 5220D(APHAAWWWA-WEF) 2005.	6,76	0,012	99,67	0,01
B P K - 5, O_2 (mg/L)	BAS EN 1899-1:2002	18,7	4,2	82,19	4
H P K , O_2 (mg/L)	Standard methods 5220-D(APHAAWWWA-WEF) 2005.	38,7	10,7	82,35	12
Total oils and grease (mg/L)	BAS ISO 11923:2002	44,35	1,3	97,07	0,1
Manganese, Mn (mg/L)	spectrophotometric P-V-26A method	1,125	0,008	99,29	0,1
Chrome (total), Cr (mg/L)	Standard methods 3111-B-(APHAAWWWA-WEF) 2005.	7,05	0,022	99,69	0,1
Nickel, Ni (mg/L)	Standard methods 3111-B-(APHAAWWWA-WEF) 2005.	0,754	0,229	89,63	0.05
Copper, Cu (mg/L)	Standard methods 3113-B-APHAAWWA-WEF 2005.	0,685	0,007	98,98	0,1
Zinc, Zn (mg/L)	Standard methods 3111-B-(APHAAWWWA-WEF) 2005.	147,5	0,043	99,97	0,2
Cadmium, Cd (mg/L)	Standard methods 3111-B-(APHAAWWWA-WEF) 2005.	0,043	0,001	86,74	0.005
Lead, Pb (mg/L)	Standard methods 3111-B-(APHAAWWWA-WEF) 2005	0,258	0,015	94,19	0,05
Iron, Fe (mg/L)	Standard methods 3111-B-(APHAAWWWA-WEF) 2005.	53,2	0,097	99,818	0,3

Table 3.The results of sample analysis before and after the treatment and the assessment of the degree of purification of "Frad" Aleksinac (the fourth quarter).

Parameter	Examination methods	Sample 1 Wastewater before the purification device	Sample 2 Wastewater after the purification device	% the degree of purification	MAC
Sedimentary matter (mL/L/2h)	Stand. methods 5220D(APHAAWWWA-WEF) 2005.	150	0	100,00	25
pH value	BAS ISO 10523.2002	5,5	7,3		6,8-8,5
Sulphates SO_2 (mg/L)	BAS EN ISO 10304-1:2002	11670	22,8	99,76	25
Unfiltered water evaporation residue (mg/L)	BAS ISO11923:2002	263290	164	99,90	100
Filtered water evaporation residue (mg/L)	BAS ISO11923:2002	252370	24,6	99,90	25
Suspended matter, (mg/L)	BAS ISO11923:2002	10920	22	99,98	30
The consumption of $KMnO_4$, (mg/L)		37920	13,9	99,96	20
Chlorides HCl, (mg/L)	BAS EN ISO 10304-1:2002	17720	14	99,92	25
Nitrates N, (mg/L)	BAS EN 10304-1:2002	7800	2,1	99,97	10
Nitrites N, (mg/L)	BAS EN 10304-1:2002	27,5	0,0075	99,98	0,05
Ammonium ion, (mg/L)	BAS EN 25663:2000	525	0,3	99,94	1
Anionic detergent. (mg/L)	Stand. methods 5220D(APHAAWWWA-WEF) 2005.	0,96	0,012	97,71	0,01
B P K - 5, O_2 (mg/L)	BAS EN 1899-1:2002	3800	4,07	99,85	4
H P K , O_2 (mg/L)	Standard methods 5220-D(APHAAWWWA-WEF) 2005.	9800	6	99,94	12
Total oils and grease (mg/L)	BAS ISO 11923:2002	471,1	0,002	100,00	0,1
Manganese, Mn (mg/L)	spectrophotometric P-V-26A method	0,393	0,004	98,98	0,1
Chrome (total), Cr (mg/L)	Standard methods 3111-B-(APHAAWWWA-WEF) 2005.	1.499	0,004	100,00	0,1
Nickel, Ni (mg/L)	Standard methods 3111-B-(APHAAWWWA-WEF) 2005.	2,526	0,040	89,98	0.05
Copper, Cu (mg/L)	Standard methods 3113-B-APHAAWWA-WEF 2005.	1.535	0,004	100,00	0,1
Zinc, Zn (mg/L)	Standard methods 3111-B-(APHAAWWWA-WEF) 2005.	88,8	0,058	99,93	0,2
Cadmium, Cd (mg/L)	Standard methods 3111-B-(APHAAWWWA-WEF) 2005.	0,35	0,001	82,86	0.005
Lead, Pb (mg/L)	Standard methods 3111-B-(APHAAWWWA-WEF) 2005	0,006	0,005	98,55	0,05
Iron, Fe (mg/L)	Standard methods 3111-B-(APHAAWWWA-WEF) 2005.	70,9	0,076	100	0,3

According to the results of analyzed parameters given in tables 2 and 3 and through a comparison of the analyzed samples (Sample 1 wastewater before the purification device with Sample 2 wastewater after the purification device), primary and secondary parameter values were obtained and they are significantly below the limit values stated in the legislation on the conditions of wastewater discharge in surface water, (Official Gazette of the Republic of Serbia number 44/2001) [17-20].

Based on the sample analysis and the obtained physical chemical parameters of treated galvanic wastewater from the technological process of galvano-chemical protection and the degree of purification which ranges between 80 and 100% the functional characteristics of the existing facility in the filter factory "Frad"Aleksinac are justified.

6. Conclusion

From the ecological engineering aspect, with the right combination of the shown physical chemical wastewater treatment steps and based on the obtained results from water which passed the described treatment a satisfactory water quality is attained, and according to the existing legislation in the Republic of Serbia this water can be discharged both into the city sewer system and surface water flows. Thus, from this point of view, the company "Frad" Aleksinac satisfies environmental and legislative requirements.

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