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Environmental Management

Efficiency of Galvanic Effluent Treatment in the city of Rio Verde-Goiás

Eficiência do Tratamento de Efluentes Galvânicos na cidade de Rio Verde-Goiás

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ABSTRACT

Anthropic impacts caused to the environment, its perception and prevention are constant objects of studies aimed at improving the quality of life. Within this comprehensive area, the contamination from the galvanization process for metals and its generated waste were evaluated in this study, because galvanization, is an effective alternative in the protection against corrosion, is also a good ally in the useful life of metal parts and although practical and profitable, this process generates a huge volume of slag. This work was intended to verify by colorimetric evaluation, electrical conductivity, and in partner laboratory, through atomic absorption spectrophotometry (AAS) the efficiency of the treatment performed in an electroplating plant installed in the city of Rio Verde-Goiás, monitoring the legal standards and those obtained in the treatment. The acid effluents with emphasis on hexavalent chromium, used in the passivation of the parts, were treated with sodium metabisulfite, keeping the final effluent within a passive threshold for disposal according to the parameters of Conama Resolution 357, and municipal environmental legislation 5090 of 2005. Supported by the legal basis, it was also proven the efficiency and the cost-benefit ratio of this method in relation to other processes researched.

Keywords: Galvanizing; Cyanide; Chromium

RESUMO

Impactos antrópicos causados ao meio ambiente, sua percepção e prevenção são constantes objetos de estudos visando melhoria de qualidade de vida. Dentro desta abrangente área, a contaminação pelo processo de galvanização para metais e seus resíduos gerados foram aqui avaliados neste estudo, pois a galvanização, é uma alternativa eficaz na proteção contra corrosão, também é um bom aliado no tempo de vida útil das peças metálicas e embora prático e rentável, este processo gera um volume de escória enorme. Este trabalho destinou-se a verificar por meio avaliação colorimétrica, condutividade elétrica, e em laboratório parceiro, através de espectrofotometria de absorção atômica (EAS) a eficiência do tratamento realizado em uma galvânica instalada na cidade de Rio Verde-Goiás, monitorando os padrões legais e os obtidos no tratamento.

Os efluentes brutos cianídricos foram tratados pelo método de cloração, onde observou-se sensível redução nos parâmetros de descarte, os efluentes ácidos com ênfase no cromo hexavalente, utilizado no apassivamento das peças, foi tratado com metabissulfito de sódio, mantendo o efluente final dentro de um limiar passivo de descarte segundo parâmetros da Resolução Conama 357, e legislação ambiental municipal 5090 de 2005. Amparados na base legal, comprovou-se também a eficiência e a relação custo benefício do presente método em relação a outros processos pesquisados.

Palavras-chave: Galvanização; Cianeto; Cromo

1 INTRODUCTION

Galvanization is present in almost every aspect of daily life, seeking to offer metal parts with an attractive final appearance, free of corrosive processes. Its performance is enormous: these are furniture parts, screws, hydraulic utensils, musical instruments, car parts, connectors, metal supports used in everyday life, among others.

"Corrosion is a chemical or electrochemical reaction, between a material, usually a metal and its environment, where its deterioration is produced making it unusable due to physical, mechanical or biological causes; its existence being in two forms: (i) electrochemical or wet corrosion, (ii) dry corrosion and oxidation." ("Part I: General Aspects of Corrosion, Corrosion Control, and Corrosion Prevention," 2020). Reduced life of goods or production parts, premature failures, are problems caused by corrosion, in addition to loss of performance.

These general aspects corroborate the use of the galvanic process for the protection of metallic material, although the operational cost, the treatment of the slag generated, and its environmental liability are relevant, as well as the loss of solubilized material in the treatment baths of the parts is also relevant, either by dragging contaminating the following baths, or unattended operations generating constant contamination in loco.

In their studies Sinha *et al.* (2021) found that, of the proportion of zinc used in galvanic processes (1 kg per m^3 of solution), 11% is retained in its slag, which generates loss of material with extreme recoverability either by hydro metallurgy

or pyro metallurgy as described by Deng *et al.* (2022, fig. 2,3,4). Kaya *et al.* (2020) report that zinc (Zn) has enormous possibilities for chemical recovery without the loss of its characteristics as a substance.

As stated by Santamaría *et al.* (2022) for every 1,600 kg of material treated by the galvanic process against corrosion, 5,000 kg of liquid waste s are generated in the treatment process, generating 3,125 kg of galvanic solid waste. The formation of chemical compounds complexed by the oxidizing agents is enormous Dong *et al.* (2022).

Although the solid waste has substantial contaminant potential, legislation and inspection bodies do not stipulate standards for the disposal of the liquid waste here generated by the treatment, causing a legal gap or loophole of enormous proportions, because the ions formed in the electroplating process and subsequently in its treatment for disposal constitute a potential risk to the environment with the formation of the contamination plume Song *et al.* (2020).

In their studies Ciesielczyk *et al.* (2017), report the environmental problems caused by metal ions from the galvanic process to the environment and biodiversity , the effects that can be caused to the pH of groundwater due to the concentrations of copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn). Thus, there is a clear requirement for removal or as much reduction as possible of these compounds from the wastewater of the galvanic process.

The environmental liability caused by the galvanic process is relevant and present as stated by Abidli *et al.* (2022), and Dwivedi *et al.* (2021), and although the legislation has advanced a lot in search of environmental protection, the negative effects caused to the environment by the slag generated in the galvanizing process are still constant.

According to Liu *et al.*, (2022) the metallic compounds of copper oxide (CuO), iron oxide III (Fe_2O_3), aluminum oxide (Al_2O_3), zinc oxide (ZnO) and titanium dioxide (TiO_2) can act as electron acceptors during the formation of organic persistent environmental free radical precursors (EPFRs); EPFRs are very reactive compounds,

usually transient due to the instability of unpaired electrons. These compounds have a long and variable half-life of resistance in the environment and are quite harmful to humans.

Basdouri *et al.*(2022), demonstrate the ease of a chemical species to form a new polymorph with a smaller structure than its parent isomorph and similar chemical capacity with a half-life sufficient to size its structure by X-ray diffraction.

CONAMA resolution 420/2009 in its articles 1, 4, 5 and 6 establishes the parameters for anthropic discharges, their consequences and penalties, while CONAMA resolution 430/2011 and Municipal Law 5090/2005 in its articles 241 and 243, stipulate the maximum allowable values for the discharge of treated effluents containing heavy metals.

In this context, the objective of this work was to show the cyanide oxidation treatment by chlorination method performed in an electrodeposition facility installed in the city of Rio Verde, the parameters achieved to comply with the above mentioned laws and the success in removing metal contaminants from liquid and solid waste from the cold galvanizing process, this is not a case study, but an investigation of sustainable responsibility with the environment and future generations.

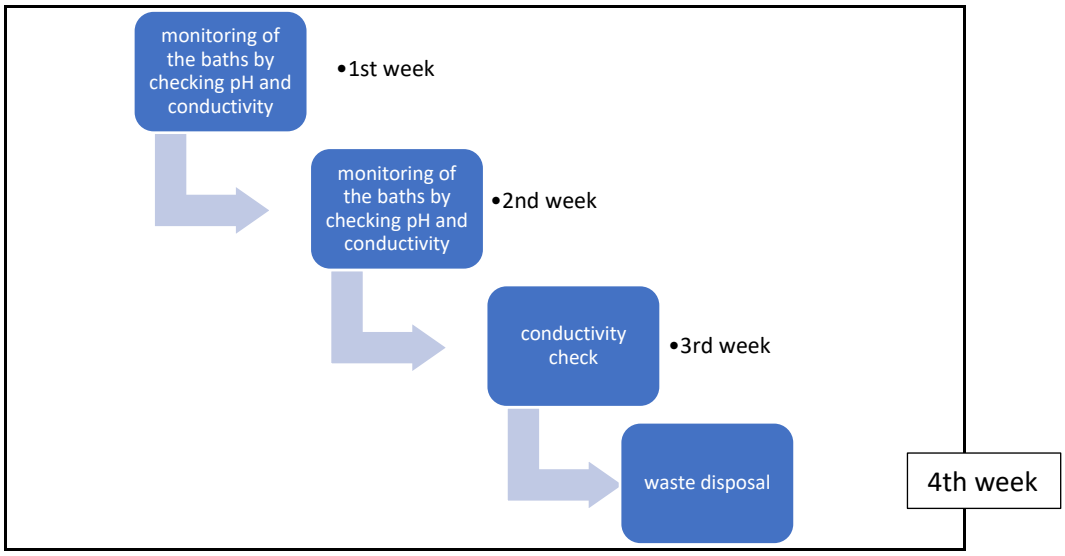
2 MATERIALS AND METHODS

The facilities of an effluent treatment plant will be used for the procedure, a direct jet compressor to keep the liquid waste in constant agitation, 12% sodium hypochlorite in canisters, 6 Mol/L sodium hydroxide solution, an anti-foaming agent, coagulant, for cyanide oxidation.

In the chromic acid reduction, a 6 mol/L sodium metabisulfite solution, hydrochloric acid for pH adjustment, again added an agent to prevent foaming, another coagulant agent for complexation of the metal compounds present. The

flow chart in Figure 1 below shows the path taken to dispose of the baths in the holding tanks and subsequent treatment

Figure 1 – Bath monitoring procedure



Source: Adapted authors

The treatment method used in the oxidation of the galvanic cyanide was by addition of an oxidizing agent, here sodium hypochlorite (ClO_3^-) was used. Cyanide or cyano is a good binder when it undergoes the action of the oxidizing agent (hypochlorite) and has a very easy formation of chlorosulfate ion, as shown in the following reaction, which was corroborated by the result of the treated effluent:

$$ClO\text{-}(aq) + H_3O+ + SO_4^{2-}\text{-}(aq) \qquad OH\text{-}(aq) + ClSO_3\text{-}(aq).; \qquad (1)$$

Sodium hypochlorite was added under constant agitation in a collection tank located at the treatment plant and the volume of liquid cyanide waste was preliminarily adjusted to pH 8 to 9 and received the 12% hypochlorite.

The procedure was as follows: The air agitation of the decanter reactor tank was turned on. 20 ml/L of an anti-foaming agent was added - when foam was present. 3.The pH of the raw effluent containing Cyanide was measured and the pH was raised, if necessary with a mixed solution of Sodium Hydroxide and 20% hydrated Lime to a value above 11.5 12% Sodium Hypochlorite solution or 10%

Calcium solution was added (Important: During the addition of the hypochlorite solution and cyanide oxidation time, the pH was kept above 11.5 with the addition of the mixed Sodium Hydroxide and Hydrated Lime solution to avoid the release of toxic gases. After one and a half hours of reaction, the free chlorine test was performed and should be positive. After the cyanide oxidation period, a colorimetric kit test was performed, and if the cyanide content was higher than 0.05 mg/L, the oxidation was continued, maintaining the presence of free chlorine until the cyanide content remained below 0.05mg/L.

For the treatment of the effluent containing hexavalent chromium with metabisulfite, we have the global equations:

$$4H_2CrO_4 + 3Na_2S_2O_5 + 3H_2SO_4 \rightarrow 2Cr_2(SO_4)_3 + 3Na_2SO_4 + 7H_2O \quad (2)$$

$$2Na_2Cr_2O_7 + 3Na_2S_2O_5 + 5H_2SO_4 \rightarrow 2Cr_2(SO_4)_3 + 5Na_2SO_4 + 5H_2O \quad (3)$$

In an acidic medium (pH up to 3.0) the reactions follow:

$$4HCrO_4^- + 3S_2O_5^{2-} + 10H^+ \rightarrow 4Cr^{3+} + 6SO_4^{2-} + 7H_2O \quad (4)$$

$$2(Cr_2O_7)^{2-} + 3(S_2O_5)^{2-} + 10H^+ \rightarrow 4Cr^{3+} + 6(SO_4)^{2-} + 5H_2O \quad (5)$$

However, despite the lower cost of sulfuric acid, the procedure was performed using hydrochloric acid to decrease the acid yield as per the following reaction:

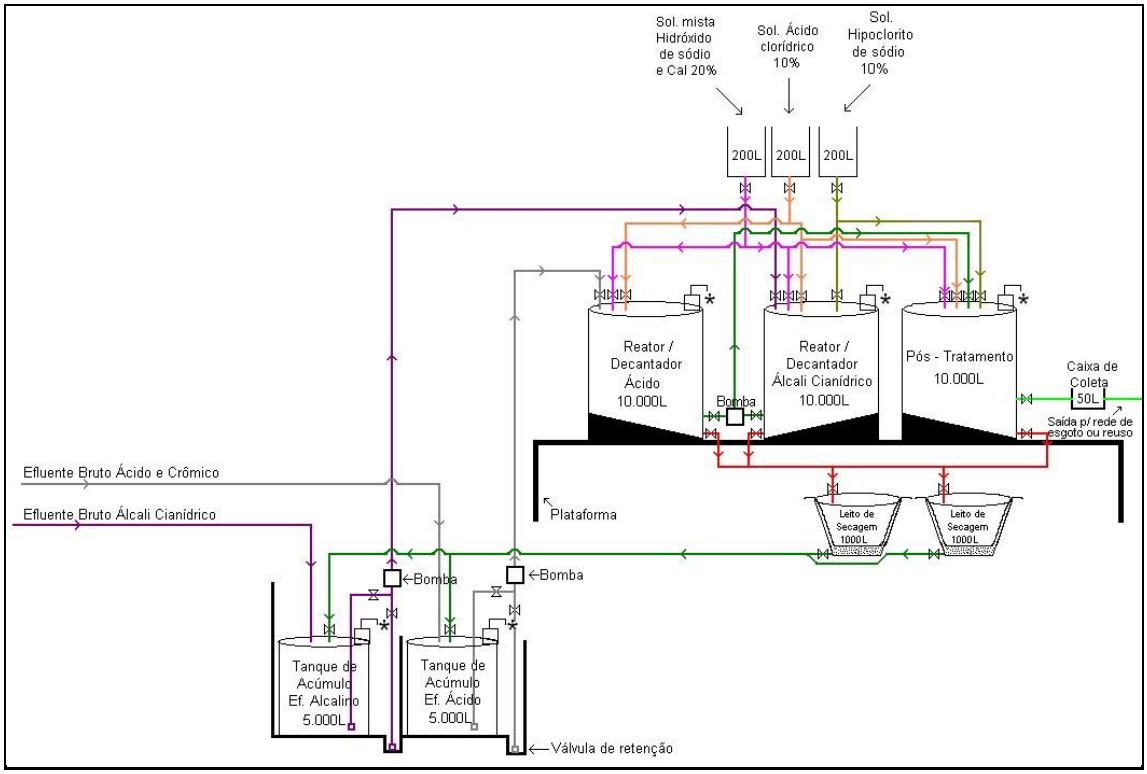
$$4H_2CrO_4 + 3Na_2S_2O_5 + 6HCl \rightarrow 2Cr_2(SO_4)_3 + 6NaCl + 7H_2O \quad (6)$$

The procedure for the treatment of the acidic effluent was as follows: 1. The air agitation of the reactor/decanter tank was turned on. 20 ml/L of defoamer was added when foam was present. 3.0 pH of the raw effluent containing Hexavalent Chromium was measured and adjusted as necessary with a 10% hydrochloric acid solution to a pH of less than 3.0 , If the Hexavalent Chromium test was positive, a 20% Sodium Metabisulfite solution was slowly added to reduce the Hexavalent

Chromium to Trivalent Chromium. During the addition of the metabisulfite solution, the pH was kept below 3.

All of these procedures were performed at the wastewater treatment plant illustrated in Figure 2 below.

Figure 2 – Effluent Treatment Plant



Source: adapted authors

After the treatment, the samples were sent to the laboratory where the following methodology was performed for opening the sample in the atomic absorption spectrophotometer. 100 mL of sample was transferred to a volumetric flask, well homogenized with nitric acid and adequately preserved so that the expected metal concentration did not suffer interference. From this stock sample, a volume of 30 mL was taken, to which 5 mL concentrated HNO_3 was added and brought to heating with glass beads, covered with watch glass, and waited to evaporate slowly over a hot plate to the smallest possible volume (about 10 to 20 mL) before precipitation. Heating was continued for complete digestion of the sample by adding 1 mL HNO_3 P.A, necessary for complete digestion as shown by

the color change of solution; care being taken not to let the sample dry out during digestion. The walls of the flask were washed with ultrapure water. There was no need to filter the sample and it was transferred to a 50 mL flask with two 5 mL portions of water and homogenized. The analysis was performed in a GBC Avanta PM double beam EAA apparatus with an eight (8) lamp tower, with programmable flame control with Acetylene/Air fuel with GBC Avanta's own software (Savant AA).

3 RESULTS / DISCUSSIONS

Table 1 below shows the values found for the treatment of the raw and treated hydrocyanic effluent

Table 1 – Raw and treated hydrocyanic effluent

Parameters	VMp/Conama 430 art. 15	Raw Effluen	Treated Effluent	units
Cd Total	0,2	0,01	<0,001	mg/L
Pb total	0,5	<0,01	<0,01	mg/L
Cn total	1,0	<0,1	<0,1	mg/L
Chlorides	NR	21.443,30	8,847,0	mg/L
Cu total	NR	0,01	<0,002	mg/L
Total Cr	0,5	0,02	0,011	mg/L
BOD	**	200	100	mg/L
COD	NR	3.264,00	987	mg/L
Tin	4,0	<0,01	<0,01	mg/L
Total Fe	NR	1,5	1,1	mg/L
Total Mn	NR	0,022	<0,007	mg/L
Mercury	0,01	<0,0002	<0,0002	mg/L
Oil/Greas	*	6,4	1	mg/L
pH	9,0	10,9	7,1	NA
Total Ag	0,1	<0,01	<0,01	mg/L
STD	NR	21,1	8,6	mg/L
SNF	NR	306	324	mg/L
SDS	1,0	1,5	0,5	mg/L
SDT	NR	2.263,00	1.158,00	mg/L
Sulfates	NR	230,2	1.307,00	mg/L
Zinc	0,001	<0,2	<0,02	mg/L

Table 1, Source: Personal collection

In table 1, for the Cadmium values, a sensible reduction in mg/L values was observed, the force exerted on the electrons in the valence layer of cadmium by

the initial exothermic reaction of the treatment for pH adjustment allows the approximation of its electronic cloud and the change of the substance:

$$Cd^{2+}_{(aq)} + 2OH^{-}_{(aq)} + e^{+} \longrightarrow Cd(OH)_2^{-} + H_3O^{+} \longrightarrow CdH^{+} + H_2O = 1{,}8\ eV. \quad (7)$$

The lead kept its initial concentration for two reasons, first its molecular orbitals did not suffer positive interference, as in the case of Cadmium, when the electronic cloud scattering in the medium, and also by small amounts of its concentration in the treatment reaction; as stated in their study LI *et al.*., (2020) the cyanide, a good ligand when it suffers the action of the oxidizing agent ClO^{-} (hypochlorite) has great facility to form the chlorosulfate ion as shown in the reaction that follows and corroborated by the result of the treated effluent:

$$ClO^{-}_{(aq)} + H_3O^{+} + SO_4^{2-}{}_{(aq)} \rightleftharpoons OH^{-}_{(aq)} + ClSO_3^{-}{}_{(aq)}. \quad (8)$$

The atomic properties such as their wave functions described by Schrodinger, the wave-particle duality, the uncertainty principle proposed by Heisenberg, the atomic radius of some elements, which is the average distance from the electrons to the nucleus and is related to the energy required to remove them in a cation formation process, also the metal radius, greatly assist in understanding the chemical reactions.

The reduction in the amount of chlorides formed is quite substantial, because the bond strength of the chloride ion as a ligand is high, thus making it easy for it to approach the electronic clouds of the transition elements, with the exception of (Zn, Cd, and Hg), and thus its total values were minimized. For the levels of copper and chromium there is a very close line of reasoning, because the energy provided by the addition of solid NaOH to raise the pH facilitates their binding forming hydroxyls of $Cu(OH)_2$ and $Cr(OH)_3^{-}$ although in the specific case of chromium in the presence of sulfates the chromium has a great facility of solubilization and formation of the chromate ion CrO_4^{2-}, highly toxic and harmful

to man and the environment. According to Figueirêdo *et al.* (2021) the generation of galvanic waste is a worldwide problem, because the trace metals present therein are of great environmental risk.

For Faramarzi et.al (2020), the cyanide leaching technique continues to be used because of its low cost, it brings with it several disadvantages, such as the increase in the treatment of its effluents, the byproduct that is the galvanic sludge, a constant need for monitoring of its physical and chemical characteristics and its generated waste, environmental monitoring through appropriate and specific legislation.

The pH value of the raw effluent serves as an interfering factor in determining the BOD, which is reduced considerably after the treatment of waste, but not enough to fit the parameters of Resolution 430/2011 CONAMA; it was not verified either in the raw effluent or in the treated effluent the formation of mercaptans, which leaves a doubt as to whether the result of the treatment produces a waste that can be discarded in this condition. The COD values found in the raw and treated effluent show a gradual reduction in the need for dissolved oxygen in the effluent which, due to lack of more current legislation on the subject, does not leave the result within the legal parameters for disposal according to (CONAMA 357, 2005), although this resolution and resolution 430/2011 do not show these rates for disposal; however, the other results in Table 1 are within the legal standards for effluent disposal.

Table 2 shows below the values of the acid effluent containing raw and treated hexavalent chromium, and the results of the acid effluent treated with metabisulfite are presented:

Table 2 – with raw and treated acid effluent values

Parameters	VMp/Conama 430art 15	Raw effluent	Treated effluent	units
Cd Total	0,2	0,01	<0,001	mg/L
Pb total	0,5	<0,01	<0,01	mg/L
Cn total	1,0	<0,1	<0,1	mg/L
Chlorides	NR	21.443,30	8,847,0	mg/L
Cu total	NR	0,01	<0,002	mg/L
Cr total	0,5	0,02	0,011	mg/L
CBO	**	200	100	mg/L
COD	NR	3.264,00	987	mg/L
Lata	4,0	<0,01	<0,01	mg/L
Fe total	NR	1,5	1,1	mg/L
Total Mn	NR	0,022	<0,007	mg/L
Mercúrio	0,01	<0,0002	<0,0002	mg/L
Óleo / gordura	*	6,4	1	mg/L
pH	9,0	10,9	7,1	NA
Idade Total	0,1	<0,01	<0,01	mg/L
STD	NR	21,1	8,6	mg/L
SNF	NR	306	324	mg/L
SDS	1,0	1,5	0,5	mg/L
SDT	NR	2.263,00	1.158,00	mg/L
Sulfatos	NR	230,2	1.307,00	mg/L
Zinco	0,001	<0,2	<0,02	mg/L

source: Personal collection

In Table 2 the results found for cadmium in the raw and treated effluent show that the system energy transfer undergone by the cadmium atom when adjusting the pH of the medium for the beginning of the treatment makes possible the reduction of its amount by positive interactions of the electrons of the atom. For lead and cyanide the values are very low, i.e., trace amounts are found.

The chlorides in the raw and treated effluent are giving an altered salinity to the system that will also alter its values of biochemical oxygen demand(BOD) and chemical oxygen demand(COD), which also have their values altered in the raw effluent and with a sensible difference in the treated effluent. These BOD and COD values will also have a direct influence on the total solids.

The formation of sulfates that are strong bonds with high penetration capacity in the dx^2 dz^2 orbitals (high spin compounds) and also dz^2 dy^2(low spin compounds) provide us with the data of reduction of the iron and manganese contents; for chromium, there was a sensible variation, which demonstrates the effectiveness of the treatment, remaining the concern with the high content of sulfates formed,

In this phase, after the treatment and preliminary rinsing, the pieces receive the passivation or brightening bath with Chromium (Cr) in a solution with nitric acid (HNO_3) and cadmium (Cd); this bath will give the metallic pieces the final appearance of galvanization. This procedure is performed with hexavalent chromium and can be done in two ways: (1) hard chromium and (2) "soft" chromium, although these two possibilities exist, the first is used more often. In work performed by Rocha *et al.*(2017) with galvanic sludge, the authors show the characterization of the sludge, its percentage of water and metals present, and its reuse at the industrial level as an aggregate in tiles, cement blocks; although the total chromium values make its use in ceramic materials unfeasible.

4 CONCLUSIONS

Although the results are satisfactory from the legal point of view, taking into account the costs of the process, such effective alternatives can also be used as Osório da Rosa *et al.*(2022), show us in their study with the use of mycotechnology for the reduction of metals in galvanic effluents, with a progress in the formation of mercaptans and also in cyanide oxidation.

The fact that the legislation has not been improved puts most of the results within the legal standards, but it is still of concern because galvanic effluents have a large metal load and drag force of these metals into the baths, thus generating very dangerous environmental assets. There is also a need for shorter disposal of

these effluents for treatment, as well as a post-treatment to be carried out on the liquid waste that remains after the steps are completed.

The use of Hypochlorite to treat cyanide has good effectiveness in reducing the contaminant, although there is a need for another oxidizing agent to be used such as another strong field ligand, thus reducing the possible coordination compounds formed during the process that could generate EPFR, which are very reactive compounds that are generally transient due to the instability of unpaired electrons. The implementation of more current treatment technology referenced in the literature can greatly increase the final quality of the environmental asset treatments generated in the electroplating process.

Post treatment or post treatment processes are presented in the formation of sub products such as the use of sulfur-based compounds in clinkerization presented by Zhang *et al*.(2018), as well as metal vitrification processes Sanito *et al*. (2022), are of uncontested relevance, myth although their operating costs require substantial technological and economic input.

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