Physico-chemical treatment of waste water contaminated with heavy metals in the industry of metallic coatings

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Abstract

This investigation was undertaken to determine the optimum conditions for physical-chemical treatment of waste water contaminated with heavy metals in the industry of metallic coatings. The industry uses substances such as: inorganic acids, alkalis, acidic and alkaline metal salts, that has a high water demand in the processes of flushing and cleaning the parts to be coated. According to the preliminary characterization of samples and reported in the literature theory, physico-chemical process was implemented for the removal of contaminants that consisted in chemical oxidation of CN-ions, followed by chemical precipitation made next to a coagulation/flocculation and subsequent adsorption on activated coal. Laboratory scale tests showed the optimal conditions of treatment including chemical oxidation by the addition of 4.15 cm^3 of H_2O_2 (30%) per gram of CN, chemical precipitation with NaOH to a pH of 12, followed by coagulation/flocculation with $Fe_2(SO_4)_3$ at a speed of 135 rpm for 3 min and 20 rpm for 20 min and finally the addition of 1.0 g of adsorbent previously activated at 700°C. From this study, it is clear that the adsorption on activated carbon is highly efficient in the removal of heavy metals from industrial waste water from electroplating. However, it is also clear that the parallel application of the treatments, shown here, is more effective to completely remove contaminants such as lead, nickel, silver, and copper at laboratory scale, so it is recommended the simultaneous use of these physico-chemical processes.

Key words: *coagulation-flocculation, heavy metals, industrial waste water, metallic coatings, precipitation*

INTRODUCTION

The industrial development has caused significant increases in the number of production processes that generate chemical or hazardous pollutants, or chemical compounds that are required as raw materials or intermediate inputs. These processes are accompanied by increasing levels of air pollutants emissions, water pollutants and a high incidence of dangerous waste; the information about the physical and chemical characteristics of the substances used in production processes can plumb to improper han-

dling by the operators and also could produce an environmental emergency, leaking, spill or explosion. In order to take action, both preventive and corrective, we made an environmental risk assessment in the industry of metallic coatings [MOLINA-GALLEGOS 2012]. The impurities that can be found in effluent from numerous sources (domestic and industrial), of different nature and concentration, and its treatment can realize by different ways [BEDLA, DACEWICZ 2019; DOMAŃSKA *et al*. 2019]; reagents that are frequently used in the processes are: inorganic acids, alkalis, acidic and alkaline metal salts, metal oxides, solvents, pol-

ishes, surfactants, among others; as a result, residues of these substances are also commonly found in sewage, even groundwater [MALEK *et al.* 2019], thanks to the drag of chemicals in the corresponding to the process rinses [TEJADA *et al.* 2014].

The pollution of industrial waste water with heavy metals is one of the most serious environmental problems that occurs today [BOLAÑOS *et al.* 2014]. Most of these products are hazardous substances, persistent and bio-accumulative, but the features mainly toxic confers the management of metals such as chromium (Cr), plumb (Pb), cadmium (Cd), nickel (Ni), zinc (Zn), silver (Ag), among others, which make this industry is one of the most dangerous for the environment, since contaminants such as heavy metals are not biodegradable, exhibit high solubility in aquatic systems and can be absorbed by living organisms [TEJADA-TOVAR *et al.* 2015]. Once they enter the food chain can be accumulated in the human body causing serious health problems [LONDOÑO-FRANCO *et al.* 2016].

The removal and/or recovery of metals has been practiced for more than 5000 years; have developed an arsenal of separation technologies both to reduce the amount of waste water generated to improve the quality of the treated effluent [TEJADA-TOVAR *et al.* 2015]. For the latter are methods of removing conventional and chemical precipitation, processes of coagulation-flocculation, flotation, adsorption, oxidation, among others, but before you opt for any of these methods must be analysed using the parameters such as the initial concentration of pollutants and the volume of effluent to be treated, since in galvanization plants qualitative and quantitative variations of pollutants are common due to the wide variety of coating processes that are given to the surface of a metal [CARDONA 2014]. It is generally recommended the separation of the waste water flows, according to their composition, in partial flows: waste water acidic, alkaline waste water, waste water with cyanide, waste water from the chrome, waste water from the degreasing. [FREIRE-ESPÍN 2012]. The advantage of not mixing different partial flows is the possibility of a specific treatment of waste water and sludge generation monometallic that can be retrieved more easily [DELGADILLO *et al.* 2010; MAZARIEGO-ROBLES 2017].

The aim of this research is the evaluate the removal to heavy metals (arsenic – As, chromium – Cr, cupper – Cu, silver – Ag, nickel – Ni and Pb, plumb) of economic interest of the waste water of the electroplating plant Argentis collection´s Ltda, with different physico-chemical treatments as a synergic system.

MATERIALS AND METHODS

The samples were collected in the electroplating plant of a company located in the city of Cucuta, Norte de Santander, Colombia, dedicated to the production of coated in silver accessories. The sampling was carried out under the principles of custody of collection, handling and transport of samples, following the recommendations of standard methods for the analysis of drinking and waste water as contemplated in the RAS 2000 [Minvivienda 2000]; for this, one sampled was carry out in the plant, between Janu-

ary and February 2010, and samples was taken with clean plastic bottles with a 1 dm^3 of capacity. The literature recommends the separation of the waste water flows and the partial treatment of these in electroplating, due to the complexity of processes and the large amount of chemicals handled, for this reason, two samples of 1 dm^3 were taken from each of the contiguous rinses the tanks of coating, to analyse a possible obtaining sludge metal, as these contain different pollutants by the drag of chemicals from the immediately preceding [FREIRE-ESPÍN 2012]. In addition, samples of the storage tank waste water treatment of the company where they are all residues of the process, without prior separation of the same and are stored until 5000 dm^3, in order to provide treatment discontinued in this water.

In synthesis, there was a single sampling in the storage tank of waste water in where all waste from the processes and samples were also taken from the subsequent rinses baths: chemical degreasing, varnish, metallic coating: copper alkaline pH, copper acid pH, palladium – tin (SnO_2), pre-silver and silver.

The concentration of metals was determined by atomic absorption spectrometry using an Atomic Absorption Spectrophotometer (AAS) Perkin Elmer Analyst 300 with hollow cathode lamps As, Cu, Cr, Ni, Pb, and Ag. The determination of silver in the water samples was performed by a metric method (since I didn't have hollow cathode lamp corresponding to this element), using potassium thiocyanate KSCN (Carlo Erba®) 0.101 M as the titrant and iron (III) chloride – $FeCl_3$ (Merck®) 0.037 M as an indicator [BUDAVARI 1989; VERARDO *et al.* 1990]. The determination of the metals was performed before and after each treatment, and concentrations values are expressed in average, and removal are expressed in percent (%).

CHEMICAL PRECIPITATION FOLLOWED BY COAGULATION/FLOCCULATION (P-C/F) WITH IRON (III) SULPHATE

Prior to these analyses, it was carried out the oxidation of cyanide content in the samples with hydrogen peroxide (H_2O_2) at the pH of 11.45 due to interference that these had to form very stable complexes with metals, which does not make it possible precipitation. The experiments started with a pH adjustment to 12 with sodium hydroxide (Carlo Erba®), for the chemical precipitation in alkaline medium of the preliminarily treated samples with H_2O_2, in an In lab Multi Level 1 equipment [VERARDO *et al.* 1990]. The tests were conducted on a universal bottle probe tool, using as a coagulant/flocculant of iron (III) sulphate ($Fe_2(SO_4)_3$) [BUDAVARI 1989]. Previously determined the best coagulant/flocculant, optimum pH as well as the speed on the tool, the universal bottle probe. The samples were restive initially for 3 min at 135 rpm and then to 20 rpm up to complete 20 min. Finally left to settle the corresponding solid in a space of 30 to 40 min.

ADSORPTION ON ACTIVATED CARBON (A)

For the study of adsorption on activated carbon samples were used in the previous step and decanted samples without any treatment. A quantity of 1.0 g was used from

the adsorbent for each testing, to 700°C previously activated by 40 min, added to 100 cm^3 of sample with constant stirring for 15 min and finally let itself interact the system lido-liquid by a space of 12 hours.

RESULTS AND DISCUSSION

The importance of taking samples from the rinses is, in fact, that even when these are part of the processes of coatings, are often discharged into the storage tank to be sufficiently contaminated as not to exercise their role of cleaning, and as such each rinse carries specific pollutants (not only heavy metals), therefore the idea is not to mix up pollutants, but on the contrary purveyors to a specific treatment to make it less complex this process and even the possibility of recovering some substances of economic interest. The determination of Cr and As yielded no detectable results for any of the samples. The concentration of Cu, Ni, Pb and Ag are shown in the Figure 1a for samples of the storage tank. The optimal dose of $Fe_2(SO_4)_3$ was 75 cm^3 for sample volumes of 250 cm^3.

The adsorption process was implemented in consequence that the percentage of removal of copper (Fig. 1a) after P-C/F (36.20%) was not effective enough so that samples fall within the norm established by Colombian Law (Decreto No. 1594, art 74) for this metal, but in the treatment with the percentage of adsorption of 98.01% removal was with which that goal was achieved.
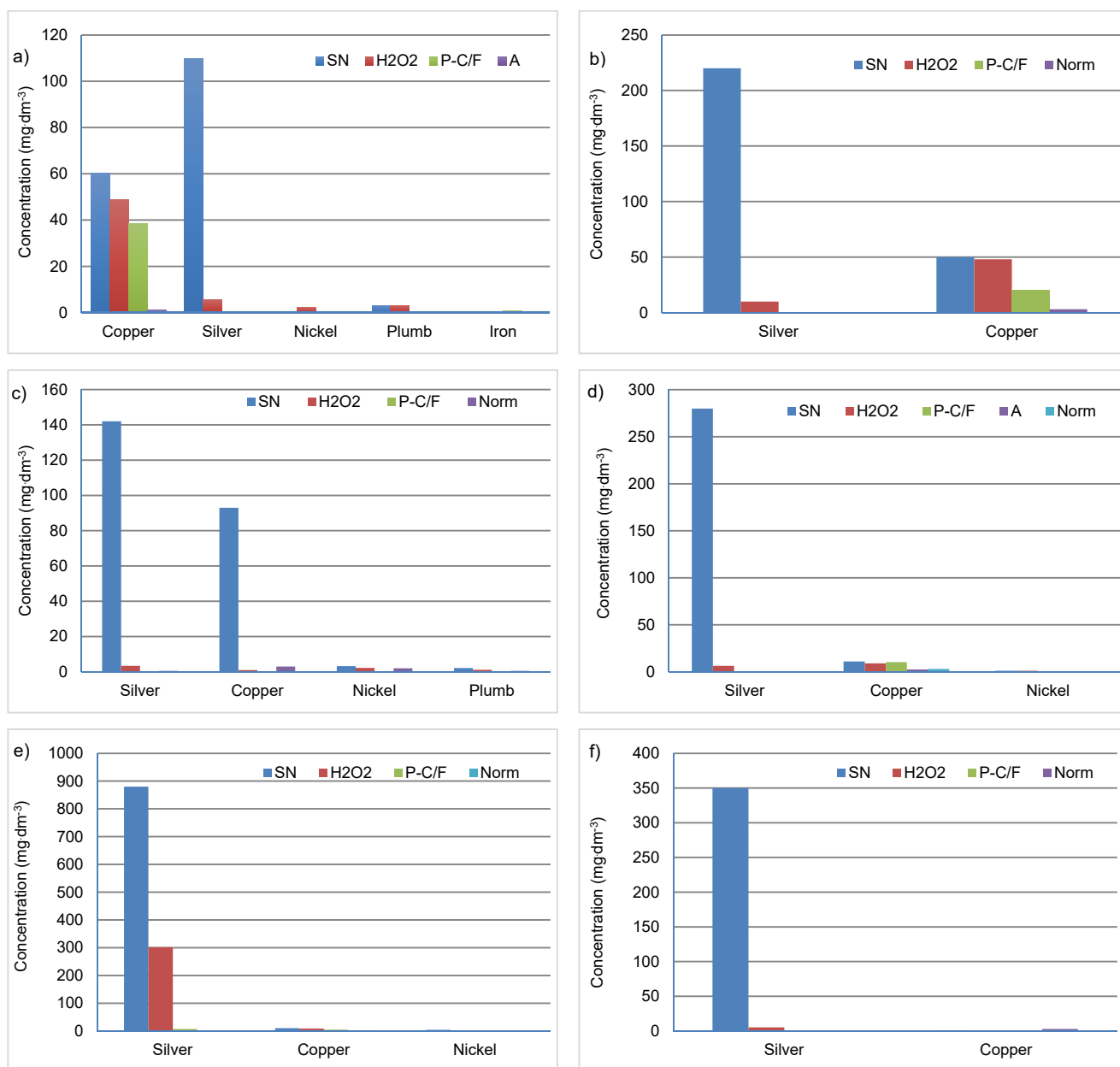

Fig. 1. Decrease of metals present: a) in the storage tank, b) in the rinse of copper alkaline pH, c) in the copper rinse acid pH, d) in the rinse palladium tin, e) in the pre-rinse of silver, f) in the rinse varnish chemical; SN = without treatment, H$_2$O$_2$ = prior oxidation of cyanide in the sample with hydrogen peroxide, P-C/F = chemical precipitation followed by coagulation flocculation, A = adsorption on activated carbon (determination not performed in these samples), Norm = values in regulation law in Colombia; source: own study

On the contrary, the silver presented a 94.85% of removal in the oxidation of cyanide with H_2O_2, even though it was intended to oxidize only the cyanide ion present in the samples, but in this procedure also adjusted the pH (data not reported), which facilitated the precipitation of metals, in the case of the metal mentioned with a high percentage of mine, which was supplemented by chemical precipitation-coagulation/flocculation. On the other hand, the results of the analysis carried out to the rinses after each bath are the following.

Copper rinse alkaline pH. As can be seen in Figure 1b the metals in this rinse are silver and copper, the percentages of mine achieved for these after all treatment were for the 100% silver and copper in tickets 87.28%. For the latter the removal was achieved thanks to the adsorption process carried out at the end. The optimal dose of $Fe_2(SO_4)_3$ was 60 cm^3 for a volume of samples of 250 cm^3.

Copper rinse acid pH. The optimal dose of $Fe_2(SO_4)_3$ was 50 cm^3 for sample volumes of 200 cm^3. For the treatment of this was not necessary to rinse the adsorption process, as shown in Figure 3 the removal was highly effective from the peroxide to the P-C/F. It shifted the 99.97% copper and silver completely. In this rinse, concentrations of nickel and plumb the order of 0.117 and 1.136 $mg \cdot dm^{-3}$, respectively, being these very low concentrations, however, it should be noted that even in small amounts the two metals are highly toxic and dangerous (Fig. 1c).

Rinse palladium tin. The optimal dose of $Fe_2(SO_4)_3$ was 40 cm^3 for sample volumes of 170 cm^3. Figure 1d shows that the concentration of copper in the sample, although important, is low in comparison with the previous rinses (only 19.77 $mg \cdot dm^{-3}$), however, as well as all the rinses the metal with a higher concentration is the silver. At the end of the treatment the three metals present fall within the rules of pollutant removal with the treatment carried out.

Pre-rinse silver. The optimal dose of $Fe_2(SO_4)_3$ was 75 cm^3 for sample volumes of 200 cm^3. As can be seen in Figure 1e, in the treatment as with the copper rinse acid pH, it was necessary to implement adsorption on activated carbon since with the P-C/F is removed the metals.

The concentration of copper and nickel is negligible while the concentration of silver is 888.22 $mg \cdot dm^{-3}$ concentration, which is reasonable since the sample comes from a rinse to where the drag of chemicals from a bath basically composed of silver salts.

Rinse silver. The optimal dose of $Fe_2(SO_4)_3$ was 40 cm^3 for sample volumes of 100 cm^3. This rinse presented a concentration of 1246.97 $mg \cdot dm^{-3}$ of silver and just 3.623 $mg \cdot dm^{-3}$ of copper as shown in Figure 1f, but even so, it became necessary to perform the P-C/F. The process of removal was one of the easiest to not possessing the interference that provide other metals for the precipitation process will take place.

Rinse chemical varnish. For this sample was not necessary to apply P-C/F, since in the pre-treatment (with H_2O_2) was removed, the concentration of metals as shown in the following. It should be noted that not all the shower in the electroplating processes presented in its formulation silver salts, for example, the copper shower acid pH, palla-

dium, the bath of varnish chemical, but from these rinses contain considerable concentrations of the precious metal, as not all bath contain copper, therefore one can speak of a possible contamination of the bath within the process.

Rinse degreaser. The samples taken from the rinse tank after the degreaser showed no detectable concentrations of any of the metals analysed. The result is acceptable, since the bath degreaser that use within the processes to clean the parts to be coated is not composed of any salt of the metals analysed in this study and also should not be contaminated by these. Additional to the previous trials, we also evaluated the reduction of pollutants to perform adsorption on activated carbon in some samples without prior treatment. As shown in Figure 2 we analysed the waste water of the storage tank of pollutants, the waters of the palladium rinse and rinse of alkaline copper. These were chosen to perform adsorption on be those rinses that needed this process after treatment with P-C/F to remove acceptable percentages of metals present in the samples.
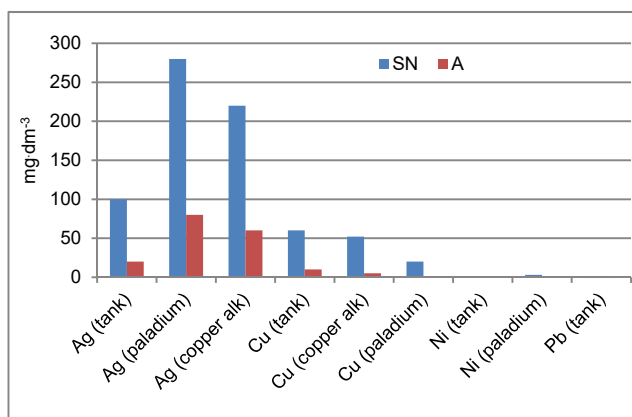

Fig. 2. Decrease in metals by adsorption for different types of samples without prior treatment; SN = without treatment, A = adsorption on activated carbon; source: own study.

It can be observed a considerable decrease in metal concentrations, the removal of silver ranged between 65 and 70% for samples of the storage tank, rinsing of palladium and rinsing the alkaline copper (% of silver mine very similar between the samples), the copper in the storage tank was removed in a 85%, 80% in the alkaline copper rinse and 97.98% in the palladium, nickel is removed completely in the samples analysed and finally plumb only in a 12.91% even when present in low concentrations, however this removal for none of the metals does not exceed the obtained using the above processes sequentially and neither leaves the metals within the permissible limits.

CONCLUSIONS

In the results it can be seen that the metals present in greater concentration on the storage tank are copper (>50 $mg \cdot dm^{-3}$) and silver (>100 $mg \cdot dm^{-3}$), as in most of the rinsing in where silver is presented in even in concentrations of 1246.97 $mg \cdot dm^{-3}$, therefore is left open the possibility of recovering this metal of high economic interest of the rinses after each coating bath instead of mixing it with

the rest of pollutants from the processes that go to the storage tank for subsequent treatment.

On the other hand, nickel is present in the samples of copper rinses acid pH, palladium and pre-silver, while the plumb in copper rinse acid pH; the two metals at low concentrations (<10 mg·dm^{-3}); therefore, it is concluded that nickel and plumb found in samples of the storage tank of waste comes specifically from the showers of the procedure.

Most important are the percentage of removal, in Cu was 98.01% with the activate carbon absorption treatment, and 99.97% of removal together with the Ag in the P-C/F treatment of the copper rinse acid pH samples; Ag presents a 94.85% of removal with the oxidation of cyanide with H$_2$O$_2$. In the active carbon absorption treatment, the percent of removal was total to Ni, and high to Cu and Ag (> 60%), but very low to the plumb (12.91%); nevertheless, only this process not allowed obtain values below the regulations of Colombia, with exception of Ni.

Implemented too many process of consecutive way to eliminate contaminants represents high cost of operation, but to waste water treatment is necessary because not all metal contaminants are removal with only one treatment, and this significant an important process to reduce the environmental contamination and risk of toxicity to worker staff.

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Fizykochemiczne oczyszczanie ścieków zanieczyszczonych metalami ciężkimi w przemyśle metalowym

STRESZCZENIE

Badania podjęto celem ustalenia optymalnych warunków fizycznego i chemicznego oczyszczania ścieków z galwanizerni. Zakłady takie wykorzystują kwasy nieorganiczne, alkalia i sole metali o odczynie kwasowym bądź zasadowym. Ponadto zużywają one dużo wody w procesie oczyszczania i płukania pokrywanych metalami elementów. Na podstawie wstępnej charakterystyki próbek i danych literaturowych wdrożono fizyczny i chemiczny proces usuwania zanieczyszczeń, który polegał na chemicznym utlenianiu jonów CN oraz chemicznym wytrącaniu, koagulacji/flokulacji oraz adsorpcji na węglu aktywnym. Testy w skali laboratoryjnej wykazały, że optymalne warunki oczyszczania obejmowały chemiczne utlenianie dzięki dodatkowi 4,15 cm^3 H$_2$O$_2$ (30%) na gram CN, chemiczne strącanie NaOH do pH 12, a następnie koagulację/flokulację z prędkością 135 obr.·min^{-1} przez 3 min i 20 obr.·min^{-1} przez 20 min oraz dodatek 1,0 g adsorbentu aktywowanego wstępnie w 700°C. Badania wykazały, że adsorpcja na węglu aktywnym jest wysoce efektywna w usuwaniu metali ciężkich ze ścieków galwanizerskich. Równoległe stosowanie zabiegów przedstawionych w pracy zapewnia jeszcze większą efektywność w całkowitym usuwaniu ołowiu, niklu, srebra i miedzi w skali laboratoryjnej. Dlatego równoczesne stosowanie tych zabiegów jest zalecane w praktyce.

Słowa kluczowe: *galwanizowanie, koagulacja/flokulacja, metale ciężkie, ścieki przemysłowe, wytrącanie*