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Ecotoxicological assessment of metal finishing effluents after real-scale treatments by conventional and advanced processes

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ABSTRACT

This study assessed the ecotoxicity and physico-chemical composition of effluents derived from a metal finishing industry after treatments by a physico-chemical process (conventional system) followed by granular activated carbon and cationic exchange (advanced system). The assessment was developed to evaluate the effectiveness of the real-scale treatment systems routinely used by the industry to reduce the pollutant content of effluents and their high whole toxicity. The results showed continuously high effluent toxicity after conventional treatments, likely caused by high dissolved salt concentrations. Due to the low frequency of reactivation/regeneration performed in the advanced treatment system and the absence of a unit operation to promote cation and anion exchange, a high content of salts has remained in the effluents. Even so, when the granular carbon was newly reactivated for treatment, great reductions in algae toxicity were found. The previous regeneration of the cationic resin also favored a remarkable toxicity reduction for algae and fish. However, most advanced treatments were ineffective in reducing chronic algae toxicity. Although the acute harmful effect for daphnid and fish has tended to decrease after advanced treatments, none of them led to the complete removal of toxicity for the evaluated organism. Several trace metals were measured in residual concentrations above the toxicity thresholds reported by other studies for similar test organisms and indicated they are also possibly contributing to the observed toxicity.

Keywords: Ecotoxicological assessment; Toxicity reduction; Metal finishing effluent; Granular activated carbon; Ion exchange

1. Introduction

The occurrence of harmful effects in aquatic organisms due the exposure to toxic chemicals present in metal finishing effluents has been reported by several studies [1–8]. The whole toxicity of metal finishing effluents reflects the interactions among multiple toxicants, such as ions and salts of metallic constituents, cyanide, polar and nonpolar organic compounds, chelating agents, surfactants and others [6,7,9].

Over the last 10 years, the legal requirement CONSEMA 129 [10] has been applied in southern Brazil to regulate the release of toxic industrial effluents into receiving water bodies. In 2010, the Environmental State Council (CONSEMA) decided to extend the compliance deadlines (CONSEMA 251) [11] due the intricacy of the technical actions to be developed and the difficulty shown by the industries to achieve

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the toxicity emission limits. Currently, the permission criteria for discharging effluents have established progressive goals to reduce toxicity that considers the lowest ineffective dilution (LID) of the effluent where no harmful effect in aquatic organisms is observed (Table 1) [10,11]. Driven by these requirements, the industries located in southern Brazil have been encouraged to continuously assess and improve their production practices and treatment processes focusing on reducing effluent toxicity [12].

As an alternative to manage this issue, the US Environmental Protection Agency provides a generalized method to structure actions focusing the reduction of whole toxicity in industrial effluents (toxicity reduction evaluation [TRE]) [13]. It should be noted that TRE programs must be developed by industries in a customized manner, given the different aims and components of each factory. However, to avoid wasting time and burdensome costs, it is coherent to obtain data that characterize the existing scenario in the initial steps of a TRE program, assessing the treatment processes available in the industry to reduce the effluent toxicity [14]. In this context, the whole effluent toxicity (WET) tests provide an effective approach to evaluate the toxicity reduction performance of treatment technologies [15], whereas WET tests depict results related to the aggregate toxic effect of all chemical constituents in the effluents, even the unknown chemicals, as well as their possible synergistic effects on test organisms [1,5]. However, some disadvantages of WET testing include the variability of the results, the uncertain level of protection of species and the inability to take into consideration bioconcentration, bioaccumulation and eutrophication in receiving streams [1,4]. Even with these drawbacks, WET testing programs have developed a significant role in reducing the toxicities of effluents being discharged into receiving waters, and improved water quality in the United States [4]. WET tests have also been widely applied in several reports assessing the harmful impact of metal finishing effluents [1–8,20].

Conventional physico-chemical (PCH) treatments have been widely applied to promote the destabilization and aggregation of particles in inorganic effluents, favoring the settling of the solid colloidal phase and the liquid phase clarification [16]. Nevertheless, effluent streams containing cyanide or hexavalent chromium (Cr(VI)) requires preliminary treatments to convert these constituents into their less toxic chemical forms and liable to be removed by hydroxide precipitation [9]. Cyanide oxidation by sodium hypochlorite and Cr(VI) reduction to the trivalent form Cr(III) by sodium sulfite are employed [7,9], followed by steps of hydroxide precipitation of soluble metals [7,9,17,18], particle coagulation by charge neutralization [17,18] and particle flocculation into large agglomerates [17,18] for subsequent phase separation. While these treatments can be used to remove the metallic constituents of effluents, they have their inherent limitations [17]. Salts are introduced during the reduction of chromium(VI) by the insertion of sodium bisulfite, resulting in an increase of the dissolved content [4]. Metallic hydroxides are amphoteric, so the pH adjustment for the hydroxide precipitation of some metals might place another metal in solution [17,18]. Moreover, coagulation–flocculation usually cannot remove all loads of heavy metals in the effluent [19]. Therefore, industries that rely on conventional treatment systems are more susceptible to the occurrence of effluent toxicity. In this context, the PCH process must be followed by advanced techniques to increase the treatment performance and the consequent toxicity reduction [20].

Advanced treatment systems functioning by adsorption in activated carbon are an alternative method of removing organic recalcitrant pollutants [1,16]. Furthermore, effluent treatments by adsorption are considered effective and economic for metal removal and can produce high-quality treated effluents [18]. The effectiveness of activated carbon for metal removal in adsorption processes can be attributed to its large surface area, high adsorption capacity and surface reactivity [17]. Ion exchange has been widely applied to remove metals from effluents, because of its treatment advantages, such as high removal efficiency and increased kinetics [17,18]. When the ion exchange is composed by unit operations of cationic and anionic exchange, significant rates of dissolved constituents can be removed [16,21]. These treatment properties might be fundamental to reduce the WET, given the fact that the toxic effects of metal finishing effluents are usually related to the presence of organic compounds [6], metals [5,6,8] and/or dissolved salts [1,4,7]. Nevertheless, no individual treatments are found to be

Table 1
Discharge permission criteria for industrial effluents in southern Brazil, modified from CONSEMA 129 [10] and CONSEMA 251 [11]

Deadline (year)	Effluent flow rate (m^3 day^{-1})				
	$Q_{max\ efl} < 100$	$100 \le Q_{max\ efl} < 500$	$500 \le Q_{max\ efl} < 1,000$	$1,000 \le Q_{max\ efl} < 10,000$	$10,000 \le Q_{max\ efl}$
2010	–	–	–	LID = 1	Absence of CT
2012	1 ≤ LID ≤ 4	1 ≤ LID ≤ 4	1 ≤ LID ≤ 4	Absence of CT	–
2014	–	–	LID = 1	–	–
2016	LID = 1	LID = 1	Absence of CT	Absence of GT	–
2018	–	Absence of CT	Absence of GT	–	–
2020	Absence of CT	Absence of GT	–	–	–
2022	Absence of GT	–	–	–	–

Note: When lowest ineffective dilution is framed within a range (e.g., 1 ≤ LID ≤ 4), the value of LID is defined by the equation $\text{LID} \le Q_{min\ rwb}/100 \times Q_{max\ efl}$, where $Q_{min\ rwb}$ is the lowest average value of the flow rates during seven consecutive days for the 10 year return period ($Q_{7,10}$). $Q_{max\ efl}$ is the maximum flow rate of the industrial effluent generated daily (m^3 day^{-1}); LID is the lowest ineffective dilution of the effluent where no harmful effect (LID) is observed in aquatic organisms; CT – chronic toxicity; GT – genotoxicity.

universally effective for this kind of effluent [17]. Therefore, it is prudent to consider that the effectiveness of these processes may vary considerably depending on the methods adopted during the treatments.

The present paper assessed the performance of a real-scale wastewater treatment plant (WWTP) at an anonymous metal finishing industry during its operational routine, while considering the parameters of PCH composition and toxicity for freshwater organisms. On the basis of the results, it was possible to identify chemical constituents that contributed to WET, the performance of the WWTP throughout its operation and to forecast the improvements needed to reduce effluent toxicity.

2. Materials and methods

2.1. Generation of effluents

The effluents were collected from a metal finishing industry located in the metropolitan region of the state of Rio Grande do Sul, Brazil. Approximately, 250 m^3 day^{-1} of non-oily effluents are generated by several productive processes conducted at this industry, such as foundry, pickling, electrolytic deburring and electroplating. A more detailed list is shown in Table 2.

The raw effluents in this industry are segregated into seven streams and sent to the WWTP, where they are stored separately in tanks with a storage capacity of 30 m^3. The raw effluents streams are segregated as a function of the characteristics of each source, related to its acid or alkali content, as well as to the presence and concentration of hexavalent chromium (Cr(VI)) or cyanide, as shown in Table 2.

2.2. Treatment of effluents

2.2.1. Assembly of batches

The effluent treatments were started by pumping the raw effluents to the inside of a batch reactor where the mixture of effluent streams and the dosing of treatment inputs were performed. The goal of this study was to provide a consistent assessment of the existing scenario in the WWTP. Thus, the four batch compositions (A, B, C and D) mixed during the routine operation of the WWTP were also reviewed in this study, as described in Table 3. The effluent stream concentrations inserted in the batch treatments (Table 3) were chosen based on a previous study [22] that evaluated feasible, frequent treatment scenarios in the WWTP and indicated the highest median toxicity of these batch compositions. Therefore, the present study considered the most critical treatment scenarios in the WWTP with regard to toxicity.

2.2.2. Conventional treatment system

The conventional PCH process starts within the reactor by the reduction of Cr(VI) to Cr(III) with sodium sulfite (10% m v^{-1}), in the cases where chromium streams constitute the effluent (batches A and B). The cyanide oxidation was performed in the effluents of batch C, using only sodium hypochlorite (12% v v^{-1}). Before combining these chemicals inputs the pH was adjusted to less than 1.5 for chromium reduction, and higher than 12 for cyanide oxidation, using hydrated calcium oxide (8% m v^{-1}), sodium hydroxide (33% m v^{-1}) or hydrochloric acid (33% v v^{-1}). Chromium reduction and cyanide oxidation were not conducted for the effluents of batch due to the absence of these chemicals in the effluents.

Table 2
Productive processes and industrial operation generators of effluent streams

Effluent stream	Productive process (raw material)									
	Foundry (aluminum)	Pickling (magnesium)		Electrolytic deburring (aluminum)	Electroplating (aluminum)					
		Acid	Alkaline		Degreasing	Acid activation	Alkaline activation	Zincate	Plating	Ion exchange
Diluted chromium acids	–	–	–	–	–	–	–	–	CRMP, RMP	–
Concentrated chromium acids	–	–	–	–	–	–	–	–	DPB, DGS, WEL	–
Concentrated acids	–	–	–	DPB, WEL	–	DPB	–	–	–	BCR
Diluted cyanide alkalis	–	–	–	–	–	–	–	DPB, RMP	–	–
Concentrated cyanide alkalis	–	–	–	–	–	–	–	–	–	BAR
Concentrated alkalis	–	–	–	–	DPB		DPB	–	–	–
Diluted acids and alkalis	WCM	DPB, RMP	DPB, RMP	RMP	RMP	RMP	RMP	–	–	BAC

Note: WCM – wash casting molds; DPB – drainage process batch; RMP – rinse manufactured piece; WEL – wash electrodes; CRMP – chromium removal from manufactured pieces; DGS – drainage gas scrubber; BCR – backwash cationic resin; BAR – backwash anionic resin; BAC – backwash activated carbon.

Table 3
Treatment batch compositions

Batch	Effluent stream	Effluent concentration[a] (%)
A	Diluted chromium acids	25
	Concentrated chromium acids	25
	Concentrated acids	50
B	Diluted chromium acids	33
	Concentrated chromium acids	67
C	Diluted cyanide alkalis	33
	Concentrated cyanide alkalis	67
D	Concentrated alkalis	75
	Diluted acids and alkalis	25

[a] Volume of effluent stream per total volume of effluents in batch treatment (%, v v^{-1}).

The next step of the PCH treatment was the chemical precipitation of metals to their low solubility hydroxides. The chemical precipitation was facilitated by adjustments of pH in the range of 7.0–8.5. The same chemical inputs inserted to adjust the pH in the first step of this treatment were also used in metal precipitation. A commercial coagulant, PAC Matryx®/Polifloc 18 (10% v v^{-1}), composed of aluminum hydroxychloride, was then slowly mixed over 10–20 min. The effluents were transferred to a decanter, where the colloidal phase was flocculated by the addition of the Matryx®/Superfloc A300 (0.1% p v^{-1}) commercial flocculant, composed of an anionic polyelectrolyte of polyacrylamide. Next, the colloidal phase was decanted for exactly 30 min. Last, the sludge was dewatered in a chamber filter press and the liquid phase was combined with previously treated effluents in a storage tank.

2.2.3. Advanced treatment system

The advanced treatment began with the transfer of the effluent from the storage tank to a filter bed filled with the Pentair®/MMFM-4872 commercial filter, composed of anthracite coal (24% v v^{-1}), sand (48% v v^{-1}), shot (6% v v^{-1}) and gravel (22% v v^{-1}). The effluents passed through the filter bed by pressurized flow in an upward direction, allowing an expansion of the filter bed to an additional 50% of its height. Then the effluents were directed to a fixed bed column filled with commercial granular activated carbon (GAC), Norit®/GAC1240W. This GAC is characterized by a total surface area of 1,150 m^2 g^{-1}, apparent density of 485 kg m^{-3}, effective particle size between 0.6 and 0.7 mm, uniformity coefficient of 1.7, ash content of 9% and humidity of 5%. The GAC underwent thermal reactivation, being heated to 800°C prior to insertion into the column for the first treatment of sampling. The effluents flowed downward through the GAC column with pressure. Once the GAC column treatment was completed, the effluents were forwarded to a fixed bed filled with a chelating cationic exchange resin (CER), Purolite®/S930Plus. The resin is composed of a polystyrene matrix and a structural exchange surface in the iminodiacetic functional group. As performed with GAC, the CER was prepared before the first treatment of sampling, through steps of acid regeneration using hydrochloric acid (5% v v^{-1}) and alkali regeneration with sodium hydroxide (4% v v^{-1}). The filter medium, the activated carbon and the resin were backwashed with demineralized water after each treatment.

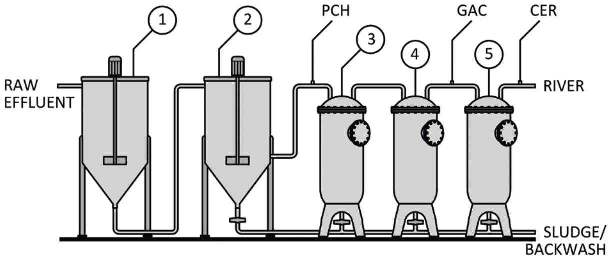


Fig. 1. Wastewater treatment system and sampling points: (1) batch reactor; (2) decanter; (3) filter bed column; (4) column bed filled with granular activated carbon; (5) column bed filled with cationic exchange resin. Sampling points: PCH, GAC and CER.

2.3. Sampling

The sampling was performed by collecting aliquots of effluents collected after PCH, GAC and CER treatments. These treated effluents were obtained throughout 12 treatments, totaling 36 tested samples (12 samples from each sampling point. During the sampling the treatments were evenly split among the compositions of batches A, B, C and D. Thus, three samples of treatments were collected and tested for each batch composition. The order of treatments was randomly assigned, according to the availability of effluents on the day of each treatment. Fig. 1 illustrates the applied wastewater treatment system and sampling points.

2.4. Collection and preservation of samples

The effluent samples originating from PCH, GAC and CER treatments were collected in separate polyethylene bottles for PCH analyses and toxicity assays. Soon after collection, the samples were stored in a secluded cooler at 4°C until arrival at the laboratories. Physical and chemical analyses, as well toxicity assays were initiated within 48 h after sample collections. Guidelines established by the ABNT-NBR 15469 [23] standard were followed for collection and preservation of the samples used in toxicity assays. The ABNT-NBR 9898 [24] recommendations were observed for the sample collection for PCH analyses.

2.5. Physico-chemical analyses

The pollutant compositions of the effluents were assessed for their PCH characteristics, nonmetallic and metallic constituents. The parameters pH and conductivity were measured immediately after sample collection using an analytical transmitter (model M400, Mettler Toledo, Columbus, USA). The total dissolved solids (TDS) were obtained by gravimetry after sample filtration (1.2 μm membrane filter) and drying at 103°C–105°C. Chlorides were analyzed by titration and following the argentometric method. Nitrates and sulfates were measured using a spectrophotometer (model SP 220, Biospectro, Curitiba, Brazil), by the chromotropic acid method and the turbidimetric method, respectively. The total organic carbon (TOC) measurements were performed by a high-temperature combustion method employing a TOC analyzer (model TOC-L, Shimadzu, Columbia, USA). Cyanide was analyzed by a colorimetric method after sample distillation, using an atomic absorption spectrophotometer (model AA240FS, Varian, Palo Alto, USA). The samples were previously digested and then the metal concentrations (aluminum, copper, chromium, nickel and zinc) were analyzed using an inductively coupled plasma-optical emission spectrophotometer (model ICP-OES, Varian). The concentration of chromium(VI) was obtained by the diphenylcarbazide colorimetric method.

Glasses and apparatus used for PCH analyses were previously acid washed. All analyses were performed according the guidelines described in Standard Methods for the Examination of Water and Wastewater [25], except for nitrate analyses, where the ABNT-NBR 12620-92 [26] was followed. The equipment and instruments used during the analytical procedures were calibrated and certified in accordance with the National Institute of Metrology Standardization ABNT-NBR ISO/IEC 17025 [27].

2.6. Toxicity assays

Chronic toxicity to the algae *Pseudokirchneriella subcapitata* was assessed according to ABNT-NBR 12648 [28] recommendations. The assays were conducted in controlled conditions of temperature (25°C ± 2°C), luminosity (4,500–10,000 lux) and continuous agitation (100–175 rpm). *P. subcapitata* was exposed to different effluent concentrations in 250 mL Erlenmeyer flasks. A blank control and a minimum of five dilutions with three replicates were provided for each assay. After 72 h of exposure to the effluents the toxicity was set by the concentration of algal inhibition growth (IC_{50}), compared with a control by graphic interpolation. The algal biomass concentration was measured in spectrophotometer at 750 nm and calculated by linear regression of the relationship between the absorbance and the number of cells per milliliter (cells mL^{-1}).

Acute toxicity in *Daphnia magna* was measured by immobility caused after 48 h of exposure to effluents according to ABNT-NBR 12713 [29]. Daphnids less than 24 h old were maintained at 20°C ± 2°C, with diffuse luminosity under a controlled photoperiod (16:8 of light:dark). Test solutions were prepared with effluent aliquots and water reconstituted for hardness between 176 and 224 mg L^{-1} of $CaCO_3$ and pH 7.8 ± 0.1. For each tested concentration four replicates were used, with five organisms each. The EC_{50} with 95% of confidence intervals was estimated after 48 h of exposure by the Trimmed Spearman–Karber method.

The toxicity to the fish *Pimephales promelas* was measured according to ABNT-NBR 15088 [30]. Fishes were exposed to the test solutions in 250 mL glass beakers with 10 organisms. The effluents were diluted in water reconstituted to pH 7.2 ± 0.2, hardness between 40 and 48 mg L^{-1} of $CaCO_3$, and kept at a temperature for 25°C ± 2°C, and under a controlled photoperiod of 16 h light and 8 h dark. Juveniles between 1- and 14-day-old, but with a difference of less than 24 h were used. A blank control and a minimum of five dilutions were used with each sample. Each dilution had 2 replicates with 10 organisms each. The toxicity of the effluents was assessed by the lethality present after 48 h. LC_{50} with 95% of confidence intervals was estimated by the Trimmed Spearman–Karber method.

In the present study, the assays with algae, daphnids and fish were similar in that they were performed in a static system without renewal of samples, the dilutions followed a geometric progression at a ratio of one half and the sensitivity to sodium chloride was assessed regularly. All toxicity assays were executed in a certificated laboratory ABNT-NBR ISO/IEC 17025 [27].

3. Results and discussion

3.1. Physico-chemical characteristics and nonmetallic constituents

Table 4 summarizes the results of physical characteristics and nonmetallic constituents of the effluents. In the present study, after treatment processes effluent pH values were kept close to neutral or slightly alkaline, suitable for a low solubility of the metallic constituents. Cyanide was present below the detection limits of the analytical method applied (cyanide < 25 μg L^{-1}) in all of the samples. This suggests the effective removal of cyanide using only sodium hypochlorite.

Table 4
Physical characteristics and nonmetallic constituents of effluents treated by conventional and advanced processes

Parameter	Unit	LOD	Conventional system	Advanced system	
			PCH (*n* = 12)	GAC (*n* = 12)	CER (*n* = 12)
pH	–	0.01	8.10 (7.76–8.61)[a]	7.78 (7.02–8.21)	8.20 (7.86–8.83)
Conductivity	mS cm^{-1}	0.001	31.4 (17.7–42.0)	31.4 (17.9–40.7)	30.6 (16.6–40.0)
TDS	mg L^{-1}	1	27,19 (13,80–36,69)	27,12 (14,05–36,94)	26,84 (13,19–37,02)
Cyanide	μg L^{-1}	25	b.d.	b.d.	b.d.
Chlorides	mg L^{-1}	1.5	4,444 (2,019–7,901)	5,198 (2,359–8,892)	5,101 (2,359–8,379)
Sulfates	mg L^{-1}	2	913 (234–1,709)	1,204 (539–2,049)	1,054 (409–1,749)
Nitrates	mg L^{-1}	0.2	198 (0.67–348)	203 (1.17–370)	228 (19.31–325)
TOC	mg L^{-1}	1.5	9.41 (4.10–14.9)	7.29 (2.01–14.5)	7.15 (1.80–14.9)

[a] Values outside the parentheses represent the average results of the four batch compositions assessed (A, B, C and D) and inside the parentheses represent their minimum and maximum results.
Note: TDS – total dissolved solids; TOC – total organic carbon; LOD – limit of detection; b.d. – below detection limits.

The toxic concentration imposed by a specific chemical constituent in an effluent (WET) may be different from the same metallic constituent dissolved in reconstituted water, in which the chemical composition of the test solution can be controlled. This variation can be caused by different assay conditions, such as: synergistic interactions among chemicals of the effluent, type and duration of exposure, the effects measured (e.g., lethality, growth, reproduction), as well as characteristics of the water or effluent (e.g., pH, hardness, alkalinity, dissolved oxygen, organic carbon) [31]. However, as it is not possible to predict the toxicity of an effluent considering only its characteristics and chemical composition; this approach can provide relevant indications of the chemicals that contribute to the whole toxicity and assist in the decision-making process about the need for improvements in the treatment system.

As noted in Table 4, high concentrations of dissolved salts were measured by conductivity and through the TDS content. High salt concentrations in metal finishing effluents often contribute to the whole toxicity [1,4,7]. The average and maximum conductivity measured after the conventional and advanced processes of the present study are similar to the values reported by Gartiser et al. [7] (24.4–39.4 mS cm^{-1}) in samples of electroplating effluents that showed high toxicity to algae, daphnid and fish eggs, even after advanced treatment (ion exchange). Beyond this case, Baral et al. [4] also found high acute toxicity levels for daphnids when a synthetic electroplating effluent was evaluated, and obtained conductivity (14.7 mS cm^{-1}) and TDS (14,810 mg L^{-1}) results close to the minimum values found in the present study.

According to the USEPA [32] significant concentrations of dissolved salts generally contribute to acute toxicity in daphnids and fishes when the conductivity exceeds, respectively, 3.0 and 6.0 mS cm^{-1}. However, through chronic toxicity assays, a conductivity of only 1.0 mS cm^{-1} for daphnids, and 3.0 mS cm^{-1} for fishes, may have harmful effects [32]. In this study, the conductivity and TDS values depict a high salt content after the treatments by PCH, which was expected due to the insertion of inputs during the production processes and treatments. Moreover, an ineffective performance of the advanced system was verified, whereby these salts were not removed from the effluents, considering the low change of conductivity and TDS after treatments on GAC and CER.

The unsatisfactory performance of the advanced system to remove the salts of the effluents was mainly due to two reasons: the first refers to the overload of salts entering the advanced system by feed streams coupled with low-frequency GAC reactivation and CER regeneration. High concentrations of salts can lead to an early saturation of the resin and the consequent clogging on active sites of ion exchange [16]. This situation requires a routine preparation of the advanced system for each treatment. However, the advanced system in single series cannot be stopped to allow the reactivation/regeneration due the high flow rate of the effluents continuously generated. Therefore, at least two sets of columns are necessary for continuous treatment in advanced system; one set performs the treatment while the other set is being reactivated/regenerated [9]. The second reason is the absence of a unit operation for the anionic exchange. Given that the chelating resin is selective for metallic cations it is possible to predict the permanence of anions dissociated in effluents, as well as bound to cations in the form of dissolved salts. Advanced systems composed of cationic and anionic exchange can achieve TDS concentrations below 2 mg L^{-1} [9]. Sapari et al. [21] assessed a plating rinse effluent treated by cationic (strongly acidic) and anionic (strongly basic) exchange resins and obtained a high performance of TDS removal (98.9%) and conductivity reduction (98.6%).

Due to the absence of an anionic exchange process, high concentrations of anion chlorides, sulfates and nitrates derived from PCH effluents were also present after the GAC and CER applications. Some treatments even caused the increase of anion contents, indicating the improper operation of the advanced system (see Table 4). The anion concentration averages verified in the present study were higher than the values disclosed by Kim et al. [6] in a metal plating effluent assessment, with respect to sulfates (698–856 mg L^{-1}), and nitrates (89.4–175 mg L^{-1}), and were far superior when compared with the values reported for chlorides (280–490 mg L^{-1}). Even so, Kim et al. [6] mention that anionic substances probably contributed to the acute toxicity in daphnids.

The content of some anions in the effluents of the present study might be contributing to the acute toxicity for daphnids. According to data disclosed by Goodfellow et al. [33] and Jo et al. [34] the acute toxicity of anionic chloride for *D. magna* (48 h) was manifested by EC_{50} values of 3,136 and 3,140 mg L^{-1}, respectively. In regards to the anionic sulfate, Scott and Crunkilton [35] also evaluated the harmful effect on *D. magna* (48 h) and found an EC_{50} of 1,194 mg L^{-1}, while Jo et al. [34] found an EC_{50} of 3,290 mg L^{-1}. Ultimately, the anion nitrate was mentioned as toxic (LC_{50} average) for *D. magna* (48 h) in 462 mg L^{-1} and for *P. promelas* (96 h) at 1,341 mg L^{-1}. However, Jo et al. [34] reported toxicity for the anion nitrate in a much higher concentration (EC_{50} 3,290 mg L^{-1}). Thus, considering the available data and respecting the toxicity variations due the assay conditions employed, it is possible to state that anionic chloride and sulfate are likely contributors to toxicity for daphnids.

After all treatment processes applied the presence of organic compounds was characterized by low TOC average concentrations (<10 mg L^{-1}), mainly if compared with the reported values of dissolved organic carbon (DOC 18.8–64.3 mg L^{-1}) in a final metal plating effluent [6]. However, residual TOC concentrations were only moderately removed with GAC treatments and maintained at similar levels after CER treatments. The contribution of refractory organic compounds to the whole toxicity should not be underestimated in assessments of effluents coming from metal finishing industries [6,7,36]. Some organic compounds have been added by the industry to the effluents through cleaning product discharges. The safety data sheets of the industry revealed the insertion of organic compounds which are highly toxic to aquatic organisms, such as dioctylphtalate for *P. subcapitata* (IC_{50} 960 μg L^{-1}) [37] and *D. magna* (EC_{50} 133 μg L^{-1}) [38], lauryl alcohol ethoxylate for *P. subcapitata* (IC_{50} 2,000–4,000 μg L^{-1}) [39] and *D. magna* (EC_{50} 6,460 μg L^{-1}) [40], 2,2'-iminodiethanol for *Daphnia pulex* (EC_{50} 2,150 μg L^{-1}) [41], among others chemicals unspecified. Additionally, Gartiser et al. [7] observed in electroplating effluents the release of degreasing agents containing alcohol ethoxylates, sodium metasilicate, fatty alcohol polyglycol ether, quaternary fatty amines and ethoxylates.

Table 5
Metallic concentrations of the effluents treated by conventional and advanced processes

Parameter	Unit	LOD	Conventional system	Advanced system	
			PCH (*n* = 12)	GAC (*n* = 12)	CER (*n* = 12)
Aluminum	µg L^{-1}	100	4,384 (2,637–7,816)[a]	2,483 (1,773–3,133)	2,556 (1,318–3,928)
Copper	µg L^{-1}	5	5,062 (1,004–17,290)	1,129 (5–2,587)	389 (5–1,431)
Chromium	µg L^{-1}	15	310 (56–1,169)	40 (15–89)	30 (15–76)
Chromium(VI)	µg L^{-1}	0.5	b.d.	b.d.	b.d.
Nickel	µg L^{-1}	8	2,435 (74–9,515)	795 (25–2,137)	361 (8–1,555)
Zinc	µg L^{-1}	100	166 (100–380)	102 (100–115)	117 (100–207)

[a] Values outside the parentheses represent the average results measured and inside the parentheses represent the minimum and maximum results.
Note: LOD – limit of detection; b.d. – below detection limits.

3.2. Metallic constituents

As shown in Table 5, high residual metal contents remained after the treatments by the conventional system, especially aluminum, copper and nickel. Sodium sulfite was able to reduce Cr(VI) to concentrations below the detection limit (<0.5 µg L^{-1}). In similar conditions of conventional treatment, but using ferric chloride as a coagulant, Saçan and Balcioğlu [5] achieved better aluminum removal of 31,000 to <100 µg L^{-1} for aluminum plating effluents. Moreover, a high variation of metal concentrations was shown throughout the present effluent assessment. This finding was also observed by Choi and Meier [2] during the evaluation of metal plating effluents from two facilities after batch treatment process, with respect to the substantial variations in the contents of copper (<50–12,800 µg L^{-1}), chromium (<50–103,600 µg L^{-1}), nickel (60–55,300 µg L^{-1}) and zinc (<50–81,600 µg L^{-1}).

Despite that the removals of salts and anions have not been effective after the advanced treatments (see Table 4), all metal contents were reduced with GAC applications. In some treatments, the use of GAC was enough to achieve the complete removal of copper, chromium and zinc. The great results obtained in the present study are consistent with other metal removal assessments through activated carbon treatments, as reported for copper [42], chromium [43], nickel [44] and zinc [45].

In addition, the treatments applying CER also favored a high performance in removing metals, except aluminum and zinc, which increased their average and maximum concentrations. The rises in aluminum and zinc content are signs that the advanced system did not operate under proper conditions, as also discussed earlier in the assessment for the reasons of the low salt removal. On the other hand, a distinguished overall efficiency using CER treatments was shown to remove copper, chromium and nickel. Similarly, by the use of macroporous resins containing iminodiacetic acid groups, Gode and Pehlivan [46] observed a great Cr(III) removal efficiency (80%–95%). The high performance of chelating resins was possibly related to their high selectivity to bind with certain types of metal cations [46].

Besides the chelating resins, other ion exchange resins can also provide high rates of metal removal. In this manner, a complete removal of chromium and zinc was obtained in a plating rinse effluent by the use of a strongly acidic cation resin and a strongly basic anion resin [21]. Using only cation exchange, nickel was removed from plating effluent at over 99% [47] and the aluminum concentration was reduced from 3,200 to 430 µg L^{-1} [34] in a pigment wastewater. Kim et al. [6] also revealed high removal of copper and nickel by cation exchange. The knowledge of the sorption equilibrium might be the key to the optimum conditions for metal removal in effluents [46].

It is also important to emphasize that though the conventional system did not provide high overall metal removal, its application is useful to protect the advanced system against overload, enabling a higher performance for ion exchange. In another study, Papadopoulos et al. [48] showed that the combination of ion exchange and chemical precipitation allowed a higher performance of nickel removal (94.2%–98.3%), when compared with a simple application of ion exchange (74.8%).

Regarding the performance of the treatment processes to accomplish the legal standards and the toxic reference limits, Fig. 2 compares the measured concentrations of metallic constituents in the effluents with the thresholds of toxicity reported in other studies for similar test organisms and the applied legal limits (CONSEMA 128) [49] to discharge effluents in receiving waters.

The analyses of metallic constituents in the effluents after conventional treatments (PCH) showed that only the emission limit for aluminum was complied during sampling. In the largest portion of the samples, chromium and zinc were within the legal emission limits, whereas copper and nickel showed concentrations above the permitted legal limits to discharge, even by their average results. Through the application of the advanced system (GAC and CER), the limits of CONSEMA 128 [49] were fully met for aluminum, chromium and zinc, except one sample (5 Å) of CER that was above the zinc concentration limit. The CER treatments allowed the compliance of the copper emission limit for the average concentration of this metal in the effluents. On the other hand, only some of the GAC and CER treatments were able to remove copper and nickel at the appropriate legal emission limits.

According to data reported by others studies (Fig. 2), on several occasions the toxicity thresholds were exceeded by the concentrations of metallic constituents in the effluents. The set of samples collected after the PCH process showed a high incidence of aluminum concentrations surpassing or close to the acute toxic threshold data published

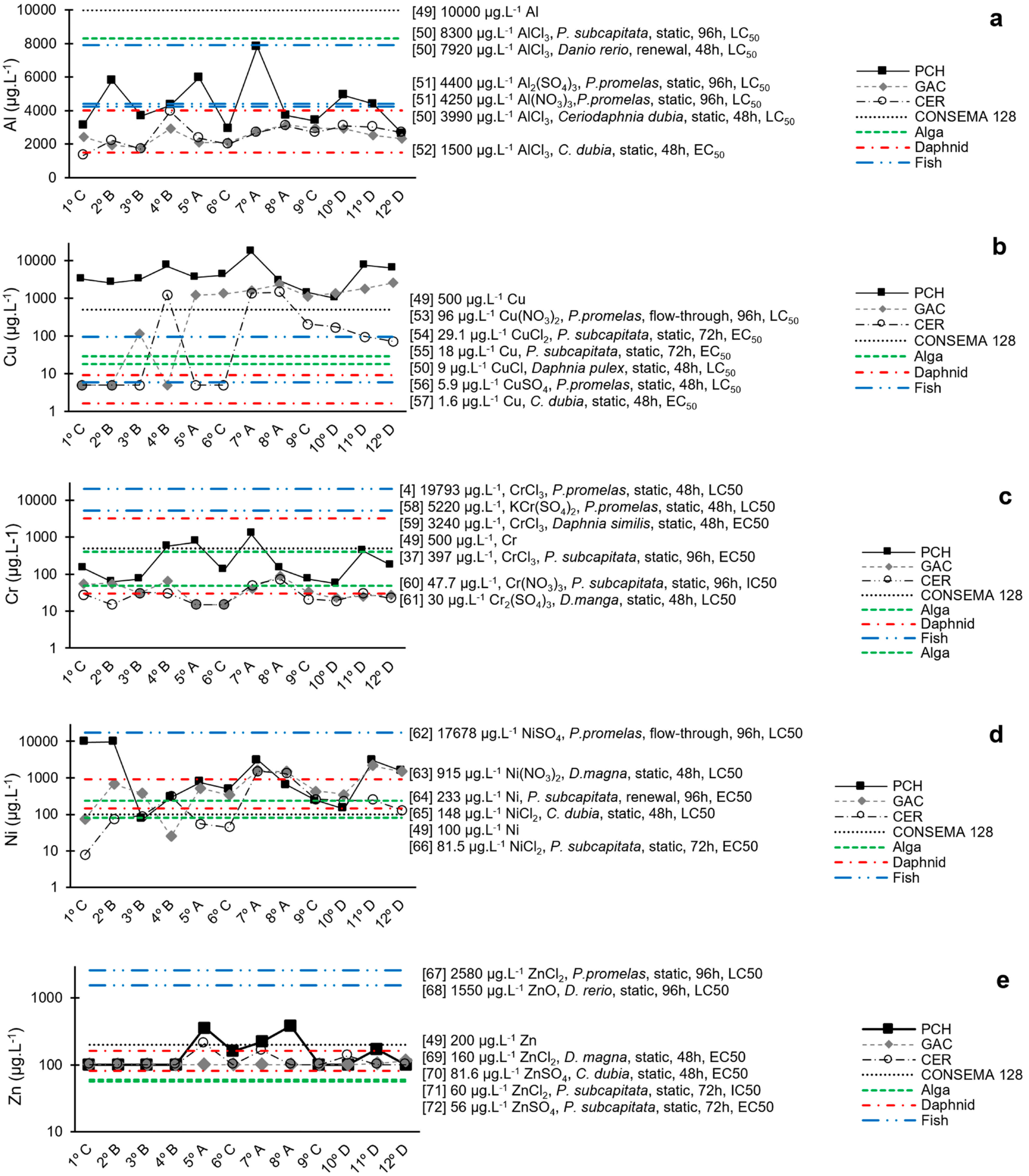


Fig. 2. Performance of the treatment processes in reducing metal contents of the effluents to accomplish the legal emission limits and the toxicity thresholds for freshwater organisms.

Note: Fig. 2 illustrates the total metal concentrations of aluminum (a), copper (b), chromium (c), nickel (d) and zinc (e) in effluents treated by the physico-chemical (PCH), granular activated carbon (GAC) and cationic exchange resin (CER) processes. These total metal concentrations are compared with the data reported from other studies related to the toxicity thresholds of specific metallic salts and ions potentially present in the effluents, as well as the limit concentrations established by the applicable legal standards CONSEMA 128 [49].

for aluminum salts [50–52]. The copper present in all of the PCH samples was well above the harmful concentrations of copper salts and dissociated copper [50,53–57]. After the PCH treatments, chromium, nickel and zinc were measured in ranges considered noncritical to acute toxicity in fish [4,58–61], though these metal contents might be potentially toxic to algae [37,62–66] and daphnids [67–72].

Regarding the application of the advanced treatment system, the fish toxicity thresholds were achieved in their entirety for most metals [4,50,51,58–61] through GAC and CER treatments. Only in few advanced treatments of the first half of sampling the copper contents were measured at levels that avoid the harmful concentrations reported for copper salt [53]. Nevertheless, the lowest copper concentrations were very close to the toxicity threshold for copper salt [56]. It is possible that copper has been removed even to lower concentrations, but the detection limit of copper measurement (5 μg L^{-1}) is not sufficient to confirm this assumption.

The proximity among detection limits of analytical methods and toxicity thresholds were also observed for dissociated copper [57] and zinc salts [65,66,72]. These findings reinforce the need for a more accurate method to measure copper and zinc during the ecotoxicological assessment.

The algae toxicity threshold [50] was met in all GAC and CER treatments except for the metal aluminum. Copper [54,55], chromium [37,62] nickel [63,64] and zinc [65,66] are also suggested to be potentially toxic for algae after several advanced treatments.

This trend of noncompliance regarding the algae toxicity thresholds was also verified assessing the data of daphnids for aluminum [52], copper [50,57], chromium [68], nickel [69,70] and zinc [71,72]. Kim et al. [6] also analyzed samples of metal finishing effluents in which the contents of copper, chromium and nickel were higher than their toxic concentrations (EC_{50}) in daphnids.

However, as the values noticed for fishes, the more expressive decreases of metal concentrations happened during the first half of the advanced treatments and also favored the compliance of the metal toxicity thresholds in algae [54,55,63,64] and daphnids [50,69,70]. This improvement was even more evident for the first treatment, where the highest removal of copper and nickel had occurred after GAC, as well as aluminum and nickel removal after CER. The second treatment also showed great performance for the metals removal, except for nickel. The higher performance in the first treatments of the advanced system to remove the metal contents may be associated with the previous reactivation of the granular carbon and the cationic exchange resin regeneration, that were provided just before the first treatment of sampling. However, it is worth nothing the substantial removal of metals on some treatments, even at the end of the sampling. The need for regular GAC reactivations and CER regenerations before the operations is reinforced by the fact that some metal concentrations either increased or remained unchanged during the period of the treatments.

3.3. Whole effluent toxicity

In the literature, several publications have reported their results of WET in different units. The present study shows the toxicity in median concentration which cause adverse effect for 50% of test organisms (IC_{50}, EC_{50} and LC_{50}), in toxic units (TUs) and as LID, according to Table 6.

As per the results of Table 6, overall, the highest toxicity was manifested in algae assays, which were also evidenced by Gartiser et al. [7] assessing metal finishing effluents. In the present study, the acute immobility of daphnids was manifested in ranges of higher effluent concentrations. The fishes were even less sensitive, though they have also been acutely affected by the effluent exposure.

According to the criteria established in a previous study [20], the toxicity generally ranged between moderate ($2 \leq TU < 4$) and expressive ($TU \geq 4$) for the trophic levels assessed in both treatment systems. Only the chronic toxicity for algae was remarkably high throughout all conventional treatments. An undefined level of toxicity has also been observed in other studies with metal finishing effluents. According to data reported by a previous study on the same Brazilian industry, but only assessing the treated effluents (72 samples)

Table 6
Whole effluent toxicity of the effluents treated by conventional and advanced processes

Trophic level (specie)	Unit	Conventional system	Advanced system	
		PCH (*n* = 12)	GAC (*n* = 12)	CER (*n* = 12)
Alga (*P. subcapitata*)	IC_{50}	0.51 (0.08–1.19)[a]	3.63 (0.12–34.47)	8.34 (0.03–46.56)
	TU_A	196.1 (84–1,250)	27.5 (2.9–833.3)	12 (2.2–3,333)
	LID_A	1,291 (128–4,096)	933 (64–4,096)	1,014 (4–4,096)
Daphnid (*D. magna*)	EC_{50}	6.34 (0.70–21.02)	16.19 (9.15–24.15)	29.79 (7.18–65.98)
	TU_D	15.8 (4.8–142.9)	6.2 (4.1–10.9)	3.4 (1.5–13.9)
	LID_D	125 (8–256)	13 (8–32)	11 (2–32)
Fish (*P. promelas*)	LC_{50}	21.40 (9.81–35.36)	38.62 (17.36–70.71)	39.90 (17.68–70.71)
	TU_F	4.7 (2.8–10.2)	2.6 (1.4–5.8)	2.5 (1.4–5.7)
	LID_F	8 (4–16)	4 (2–8)	5 (2–8)

[a] Values outside the parentheses represent the average toxicity and inside the parentheses represent the minimum and maximum toxicity.
Note: IC_{50}, EC_{50}, LC_{50} are median effective concentration of the effluent (%) which caused adverse effect for 50% of test organisms; $TU_{A,D,F}$ is the toxic unit (100 IC_{50}^{-1}, or 100 EC_{50}^{-1}, or 100 LC_{50}^{-1}); $LID_{A,D,F}$ is the lowest ineffective dilution of the effluent which the number of affected organisms was less than 10% for daphnid and fish, or 20% for alga.

of the conventional system, the acute toxicity assays for *D. magna* also indicated high variability for the median toxic concentrations (EC_{50} 0.48–100% or TU 1–208.3), though samples with expressive toxicity (TU ≥ 4) have been observed more frequently [20]. Gartiser et al. [7] also reported a study assessing more than 4,100 tests done in Germany over the years 1993–2007 with metal finishing effluents. If the median results of toxicity assays are considered, just moderate toxicities (LID 1–2) were verified for algae (*Desmodesmus subspicatus*), daphnids (*D. magna*) and fishes (*Leuciscus idus*). On the other hand, if the maximum values are taken into account, an expressive toxicity is revealed in alga (LID_A 3,072), daphnid (LID_D 512) and fish (LID_F 512). Choi and Meier [2] found a high variability on the harmful effect of metal plating effluents after conventional treatment (simple pH adjusts), given the ranges of acute toxicity for *D. magna* (EC_{50} 0.01%–100% or 1– 10,000) and *P. promelas* (LC_{50} 2.38%–100% or TU 1–42).

Even after the advanced treatments the toxicity may range considerably and reach expressive levels. In this context, Gartiser et al. [7] also disclosed values ranging from LID_A 6–16,384, LID_D 1–128 and LID_F 1–1,024 (fish egg assay), for quite similar samples of electroplating effluents treated by PCH process followed by ion exchange. It is noteworthy that the effluent samples with maximum toxicity were the same as those presenting the highest conductivity (24.4–39.4 mS cm^{-1}) [7].

In addition, other studies found high acute toxicity in metal fishing effluents, such as reported for *Daphnia similis* (EC_{50} 2.9%–7.9% or TU 12.7–34.5) after resin exchange process [3]. By evaluating the exposure to diluted electroplating effluents, the immobility of *D. magna* was found as LC_{50} 17% or TU 5.9 [4], and for fish *Oreochromis mossambicus* as LC_{50} 4% or TU 25 (96 h) [8]. Kim et al. [6] also reported a TU between 9.9 and 13.3 after exposed to final metal plating effluents for *D. magna*. These results were consistent with the high content of toxic constituents remaining in some metal finishing effluents and warn about the need for high treatment efficiency.

Fig. 3 presents the performance of each treatment to reduce the WET. Overall, after the use of the GAC treatments, the acute toxicity for daphnids and fish tended to decrease in variating performances. On the other hand, the applications of the advanced system resulted only in weak changes of TU for algae, both by GAC and by CER. Although the CER process has shown inconsistent toxicity reductions for daphnids, this effect was not observed for fish. As shown for algae, the fish assays indicated that in several treatments with CER, the toxicity increased slightly or remained the same. This inneffective perfomance of some advanced treatments to remove the toxicity was understandable, considering the occurences of rises and changes of metal contents. Moreover, it should be noted that none of the treatments promoted the complete removal of toxicity for algae, daphnids or fish. This finding reinforces the needed for improvements in the advanced treatment to ensure the removal of acute and chronic toxicity.

The treatments conducted at the beginning of sampling favored higher performance to reduce algae and fish toxicity. In the first treatment, the removal of toxicity for algae was highest after treatment with GAC (ΔTU 280.7). In the second treatment, only the CER allowed a substantial reduction of algae toxicity (ΔTU 150.1). The high concentration of nickel after GAC in the second treatment (Fig. 2) may explain the low reduction of algal toxicity. Through CER treatment, the lethal effect for fish was only reduced in the first treatment (ΔTU 1.4). It is worth considering that only the first treatment reduced the toxicity consistently for all trophic levels, by both GAC and CER.

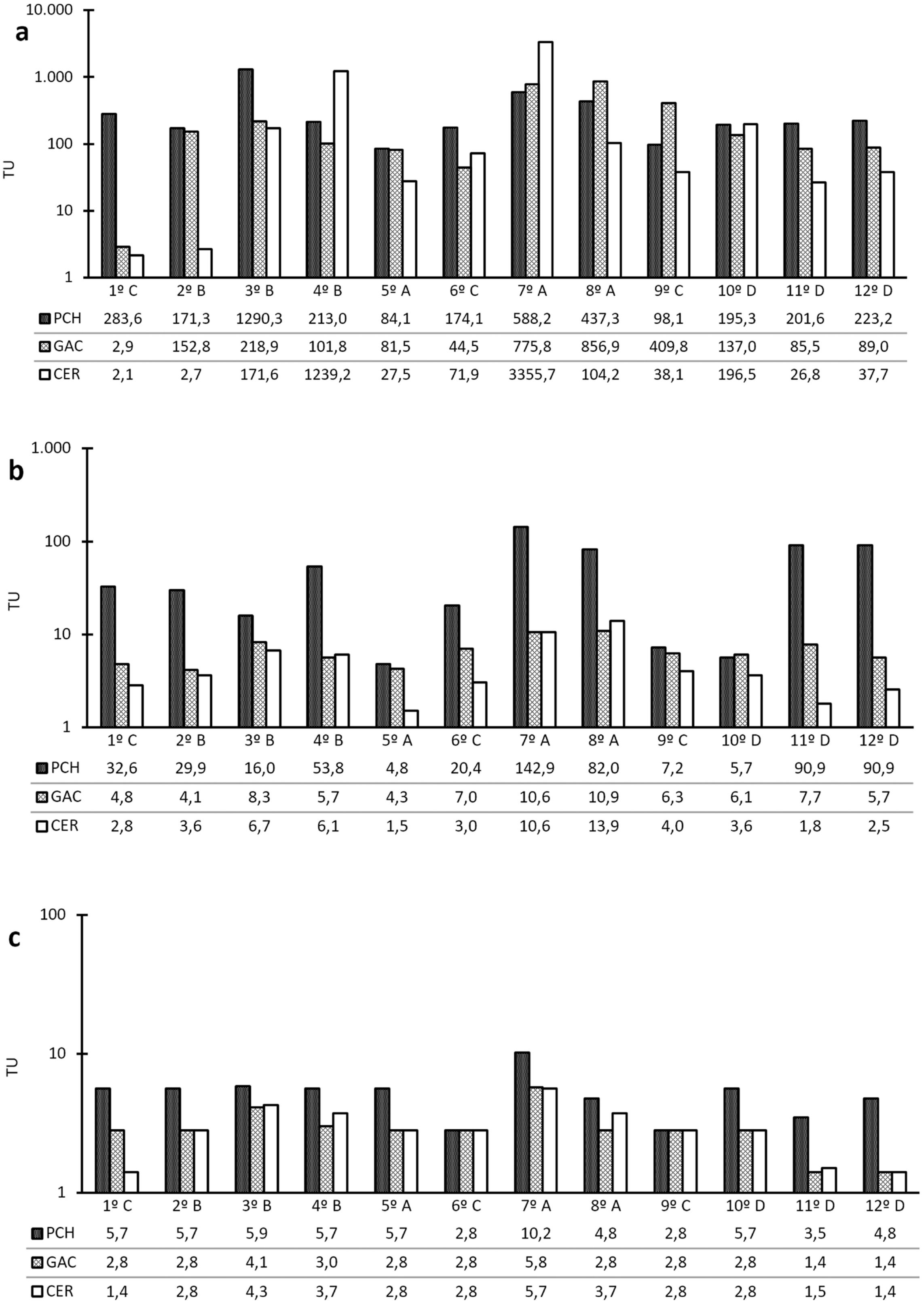
Although the TU for daphnids was moderately reduced by GAC in the first treatment, a similar performance was seen in other treatments. The reduction of toxicity for daphnids noticed after CER and for fish after GAC were even higher on the intermediate and final treatments during sampling. This finding suggests that the GAC reactivation and CER regeneration did not exert a distinguished increase of performance to remove the toxicity for fish and daphnids, respectively. However, a remarkable performance was verified after other treatments with CER, as the reduction of the TU in ΔTU 132.3 for daphnids. The most promising treatment with GAC for fish toxicity allowed a reduction of the TU in ΔTU 4.4.

In the literature, Kim et al. [6] assessed metal plating effluents and achieved high effectiveness (nearly 90%) in reducing toxicity for *D. magna* with C18 SPE sorbent (solid extraction phase). When evaluating another sample for the same industry, the toxicity for daphnids was reduced from 5.3 TU after filtration and decresed to 1.0 TU after cation exchange [6]. In the present study, the advanced treatments were useful to decrease the toxicity for some trophic levels, though it seems essential to remove the salt and anionic content to eliminate the toxicity. In a similar context, Mount and Hockett [1] assessed an electroplating effluent and found that acute toxicity in *Ceriodaphnia dubia* was not reduced by treatment with activated carbon or cationic exchange, but with both cation and anion exchange toxicity was removed completely.

4. Conclusions

This study provides consistent ecotoxicological data and PCH composition of metal finishing effluents after treatments by conventional and advanced processes. High contents of dissolved salts were found in the effluents after PCH treatments and persisted even after the application of GAC and cationic exchange resin. The ineffective removal of salts from the effluents by advanced treatments was mainly caused by the underestimated loads of salts that entered the treatment system, the low frequency of GAC reactivation and CER regeneration, as well as the absence of a treatment process able to exchange anions with the effluent.

The conventional PCH process was unable to assure the compliance of the legal emission standards for copper, chromium, nickel and zinc. Moreover, for all trophic levels evaluated, the concentrations of the metallic constituents in PCH effluents exceeded the toxicity thresholds reported by other studies. After the advanced treatments by GAC and CER processes, the emission standards for chromium and zinc were met, but they were not for copper and nickel. The decreases of metal concentrations with advanced treatments allowed for the fish toxicity thresholds to be met for all metallic constituents evaluated, except for copper. The toxicity thresholds for daphnids suggest a potential acute effect owing to the effluent concentrations of aluminum, copper, chromium, nickel and zinc. Among these metals, algae were not affected only by the aluminum toxicity values.



a

	1º C	2º B	3º B	4º B	5º A	6º C	7º A	8º A	9º C	10º D	11º D	12º D
▩ PCH	283,6	171,3	1290,3	213,0	84,1	174,1	588,2	437,3	98,1	195,3	201,6	223,2
▨ GAC	2,9	152,8	218,9	101,8	81,5	44,5	775,8	856,9	409,8	137,0	85,5	89,0
☐ CER	2,1	2,7	171,6	1239,2	27,5	71,9	3355,7	104,2	38,1	196,5	26,8	37,7

b

	1º C	2º B	3º B	4º B	5º A	6º C	7º A	8º A	9º C	10º D	11º D	12º D
▩ PCH	32,6	29,9	16,0	53,8	4,8	20,4	142,9	82,0	7,2	5,7	90,9	90,9
▨ GAC	4,8	4,1	8,3	5,7	4,3	7,0	10,6	10,9	6,3	6,1	7,7	5,7
☐ CER	2,8	3,6	6,7	6,1	1,5	3,0	10,6	13,9	4,0	3,6	1,8	2,5

c

	1º C	2º B	3º B	4º B	5º A	6º C	7º A	8º A	9º C	10º D	11º D	12º D
▩ PCH	5,7	5,7	5,9	5,7	5,7	2,8	10,2	4,8	2,8	5,7	3,5	4,8
▨ GAC	2,8	2,8	4,1	3,0	2,8	2,8	5,8	2,8	2,8	2,8	1,4	1,4
☐ CER	1,4	2,8	4,3	3,7	2,8	2,8	5,7	3,7	2,8	2,8	1,5	1,4

Fig. 3. Performance of the treatment processes to reduce whole effluent toxicity.
Note: Fig. 3 shows the results of chronic toxicity in alga (a), and acute toxicity in daphnid (b) and fish (c) after exposure to the physico-chemical (PCH), granular activated carbon (GAC) and cationic exchange resin (CER) treatments. The results are presented in toxic units (TUs) = (100 IC_{50}^{-1}, or 100 EC_{50}^{-1}, or 100 LC_{50}^{-1}).

The WET was high for all freshwater organisms assessed after conventional treatments. On the other hand, the advanced treatments reduced the WET to reasonable levels, mainly for daphnids and for fish after GAC, though none has removed it completely. Algae were the most sensitive organism to the effluents, and high toxic concentrations persisted after advanced treatments. The GAC reactivation and CER regeneration contributed significantly to a better treatment performance to remove copper, nickel and the toxicity for algae. Additionally, the CER regeneration also favored a high removal of fish toxicity.

5. Recommendations and perspectives

The simple application of the conventional treatment system could not remove the high toxicity identified for all evaluated test organisms (alga, daphnid and fish). Both advanced treatment processes provided reasonable reductions of the acute toxicity for daphnid and fish. When the GAC and the cationic exchange resin were prepared through reactivation and regeneration, respectively, chronic algal toxicity reduction was also possible. Therefore, preparation of the advanced system is highly recommended to reduce algal toxicity.

None of the advanced treatments performed could completely remove the effluent toxicity. The permanence of excessive salt concentrations in the treated effluents was a likely cause for this persisting toxicity. Thus, in this case, we recommended adding an anionic exchange resin in the advanced treatment system to evaluate the reduction of the effluent toxicity.

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