

Toxicity Identification Evaluation (TIE) of CENIBRA's Internal Effluents

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ABSTRACT

CENIBRA's non treated effluent has presented acute toxicity (MICROTOX) and, when it is launched in the waste water treatment plant (WWTP), it may cause damage to the microbiota of the activated sludge and, consequently, reduce the WWTP effectiveness. In order to avoid the decrease in the performance of WWTP, we opted for searching the main causes of toxicity in the sectorial effluents of CENIBRA. Then, it was decided to apply the TIE (toxicity identification evaluation) technique, which allows the identification of the main compound groups that cause toxicity, to six different sectorial effluents of CENIBRA. This work was made in 2003 and brought as results indications of the main villains of toxicity in each effluent, as well as suggestions of actions to be taken to reduce toxicity.

KEY-WORDS: TIE, ACUTE TOXICITY IDENTIFICATION, EFFLUENTS, MICROTOX

INTRODUCTION

CENIBRA's sectorial effluents have presented acute toxicity to the organism *Vibrio fischeri* (MICROTOX). These effluents once launched in the WWTP (waste water treatment plant), may impact the treating microbiology of the effluent and, then, reduce its effectiveness (Orr et al, 1996), which makes it possible to generate treated effluents that still contain toxic compounds. There are several ways to reduce toxicity in an effluent, and they may be from simple actions to great value enterprises. Most of the companies search for alternatives to reduce toxicity; however, as these alternatives are random, they may, even after great investments, not bring the expected feedback and the effluent may still be toxic.

The TIE is a technique that was developed in the 80s and it was registered by the EPA in the U.S.A. in 1985 for acute tests and in 1991 for chronic tests. TIE is a process through which some toxic agents present in a sample are characterized and identified (Pelletier et al, 2001). TIE consists of a series of steps in which a sample is fractioned and the toxicity is isolated by groups of contaminants, such as metals (Burgess, 2000).

The greatest benefit of TIE is the identification of the compound or group of compounds, inside the effluent (Rumbold & Snedaker, 1999; Carr et al., 2001; Burgess et al., 2000;

Anderson *et al.*, 2003), that may cause toxicity (Nipper, 2000), which permits to take fast an direct decisions for its reduction. It is a technique that has been used by several industries, including the pulp and paper mills in the U.S.A., Japan and Canada, because of requirements from the environmental units, or simply foreseeing future tendencies. They are also used in sectorial effluents, in order to cause lower impact to the microbiology of the WWTP and, consequently, to its effectiveness.

There are many published studies on TIE with effluents of pulp and paper mills. Part of these studies have been made by NCASI (study center that is specialized in emissions of pulp and paper plants) in the U.S.A.. Cook et al (1998) present a summary of nine essays. Cherr and the coauthors (1987) used TIE to investigate the cause of toxicity in the effluent of a Kraft bleached pulp factory.

ANALYSIS METHODOLOGY

TIE technique – Phase I was applied to the following effluents of CENIBRA: high charge I, high charge II, evaporation II, bleaching I, acid bleaching II, alkaline bleaching II. The test was made in two occasions, in August and September of 2003.

The methodology used for the manipulation of the effluent samples was made according to the manual of EPA (1991). The manipulations were made comprehending aeration, pH variation, filtering, EDTA and tiosulphate addition.

There was a difference between the manipulations made in August and the ones made in September/ 2003. In August, all samples that had pH shock had not been corrected later, while in September, all the samples the suffered pH shock had their values adjusted again for the initial pH (ipH). The manipulations were kept in cold chamber until the moment of their acute toxicity analysis to the bacteria *Vibrio fischeri*.

The effluents were also analyzed physical and chemically by the laboratory of CENIBRA concerning the parameters pH, conductivity, real color, turbidity, COD, TRS, oxidants, AOX, sodium, SST, according to the methodology of APHA (1998).

RESULTS AND DISCUSSION

The results of the physical-chemical analysis of the effluents are found on Table 1.

The pH of High Charge II and Evaporation are the most stable, while the High Charge I and Bleaching I, the most unstable.

Table 1 – results of the physical-chemical analysis of the sectorial effluents at CENIBRA, obtained from the samplings of August and September/ 2003.

Parameter		High Charge		Bleaching 2		Evaporation 2	Bleaching 1
		1	2	Ácid	Alcaline		
pH	Aug/03	5,9	9,0	4,4	10,6	9,6	9,8
	Sep/03	7,5	9,1	6,1	9,9	9,4	6,8

Conductibility (mS/cm)	Aug/03	4,17	3,48	3,24	3,73	0,08	4,27
	Sep/03	3,01	4,59	2,78	4,15	0,14	4,21
Real color (uH)	Aug/03	1203	950	741	344	32	915
	Sep /03	937	487	307	512	57	1164
Turbidity (uT)	Aug/03	63,8	357	374	387	3,05	68,4
	Sep /03	67,7	61,7	1001	1120	2,91	51,5
COD (mg O₂/L)	Aug/03	1510	1181	1312	928	2216	1548
	Sep /03	1014	969	720	898	1980	1480
AOX (mgCl⁻/L)	Aug/03	9,82	10,08	15,02	9,95	<0,010 *	8,83
	Sep /03	5,13	4,63	8,27	4,19	<0,010 *	9,69
Sodium (mgNa⁺/L)	Aug/03	718	916	661	631	1,5	988
	Sep /03	825	977	555	895	1,5	906
SST (mg/L)	Aug/03	164	628	723	814	1	222
	Sep /03	161	314	1885	1688	-	159

The conductivity was low in all effluents, especially the evaporation effluent. The effluents from High Charge I and Bleaching I were the ones that presented highest values in color, while the Evaporation presented the lowest values. As for the turbidity, the effluents Bleaching II, acid and alkaline, had the highest values, and again the Evaporation with the lowest. Now, for COD, the effluent Evaporation was the one with highest values. The same happened to the numbers of TRS. As for AOX, the effluent that most contributed was Acid Bleaching II. The numbers of total suspense solids were very similar to the turbidity ones, detaching Bleaching II, acid and alkaline. As for the sodium, the numbers were very similar, except for the Evaporation, which had extremely low level.

*ACUTE TOXICITY TESTS WITH *Vibrio fisheri* (MICROTOX)*

a) High Charge I

The TIE made in August (Figure 1) with the High Charge effluent showed a reduction of toxicity of EC50= 11,5% (baseline) for 41& in the sample manipulated with pH shock for two hours in alkaline pH. The manipulations that the effluents High Charge I had in pH 11, and then were filtered or aerated also had their toxicity reduced. However, it was no better than the sample that had only its pH elevated. According to Hall (1996), the reduction of toxicity by pH raise, is much probably due to the presence of heavy metals that have its solubility reduced in alkaline ambience.

In September (Figure 2), it was verified that several manipulations reduced the toxicity of this effluent and the aeration of the effluent in pH 11 (probably volatile compounds are formed at this pH and they are more easily volatilized in the aeration) reduced from 30% to 60%, the

filtering of the effluent in pH 3 (probably hasty compounds are formed at this pH, that are kept in the filter) reduced from 305 to 56%, and the EDTA addition (indicates presence of heavy metals) reduced from 30% to 60% and the addition of tiosulphate (indicates presence of oxidants) reduced from 30% to 56%.

The effluent manipulation with only one filtering without pH change did not provide the effluent quality improvement, which was already expected, once this effluent presents low numbers of turbidity and SST.

Cook et al (2003) quote that the effluent of a pulp factory that presented very similar symptoms top these for high charge I, with reduction of toxicity with filtering, aeration, pH shock, EDTA and tiosulphate, had it main toxicity cause diagnosed: the heavy metals.

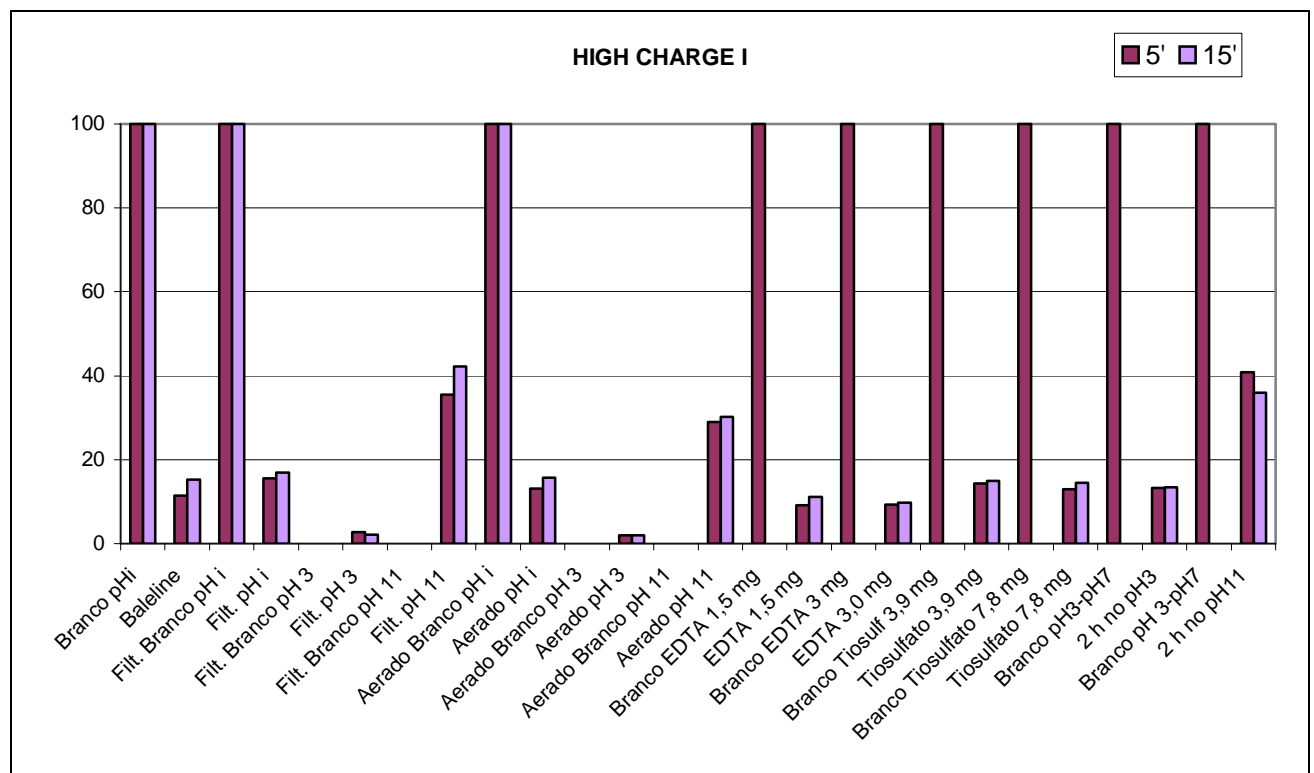


Figure 1 – Toxicity test results with the effluent High Charge I in August /2003.

White (ou Bleached) pH – branco pH

Baseline- havia baseline ao longo do texto, não baleline (vcs sabem o certo!)

Filtering pH- filtragem pH

White filtering pH3- branco filtragem pH 3

White Aerated pH 3- branco aerado pH 3

White Tiosulphate 3,9mg- branco tiosulfato 3,9 mg

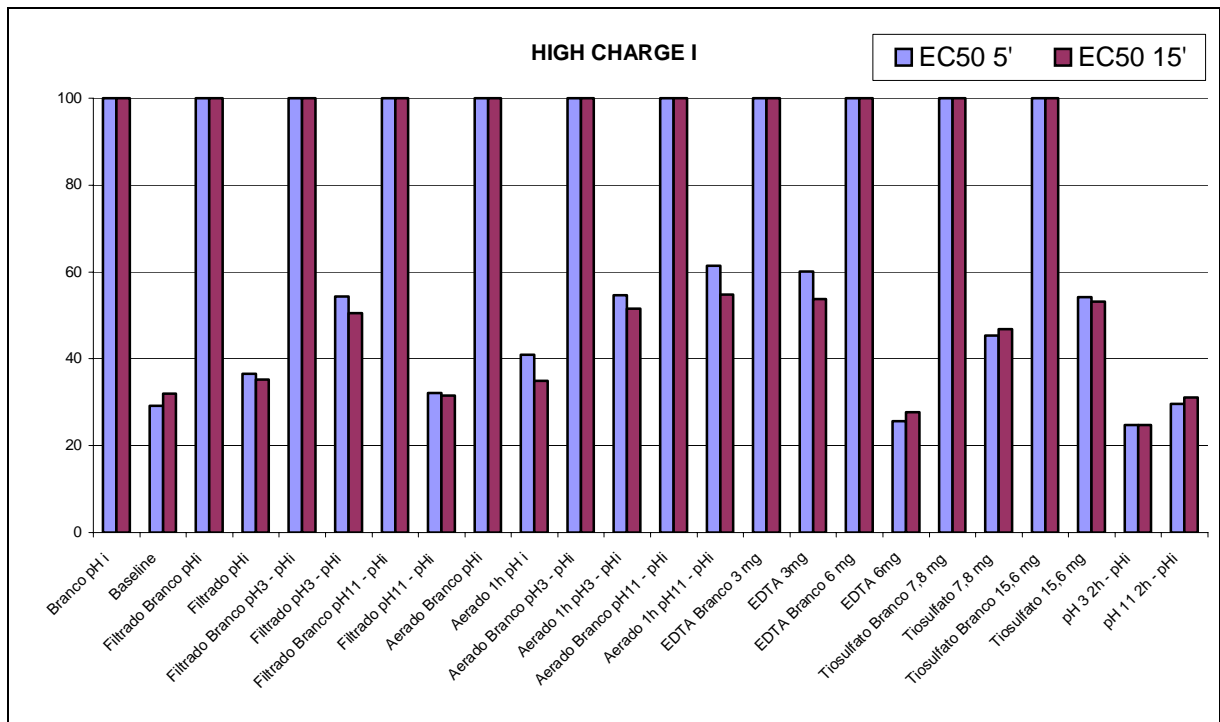


Figure 2 – Toxicity test results with the effluent High Charge I in September /2003.

b) High Charge II

The TIE made in August of 2003 with the effluent High Charge II (Figure 3), showed reductions of toxicity from 20% to 60%. The most meaningful manipulations were: filtering, which reduced from 20% to 40%; tiosulphate addition, which reduced from 20% to 56%, and pH shock to acid for two hours and back to initial pH, which from 20% to 60%. This analysis showed the presence of surfactants (filtered) and oxidants (tiosulphate) in the effluent.

In September of 2003 (Figure 4), the sample was more toxic (baseline) and the manipulations did not reduce much the toxicity, being possible to rebound only the effluent that had its pH acidified to 3, was filtered and then had its pH restored to the initial level. This manipulation reduced toxicity from 10% to 30%. The tiosulphate also reduced toxicity a little.

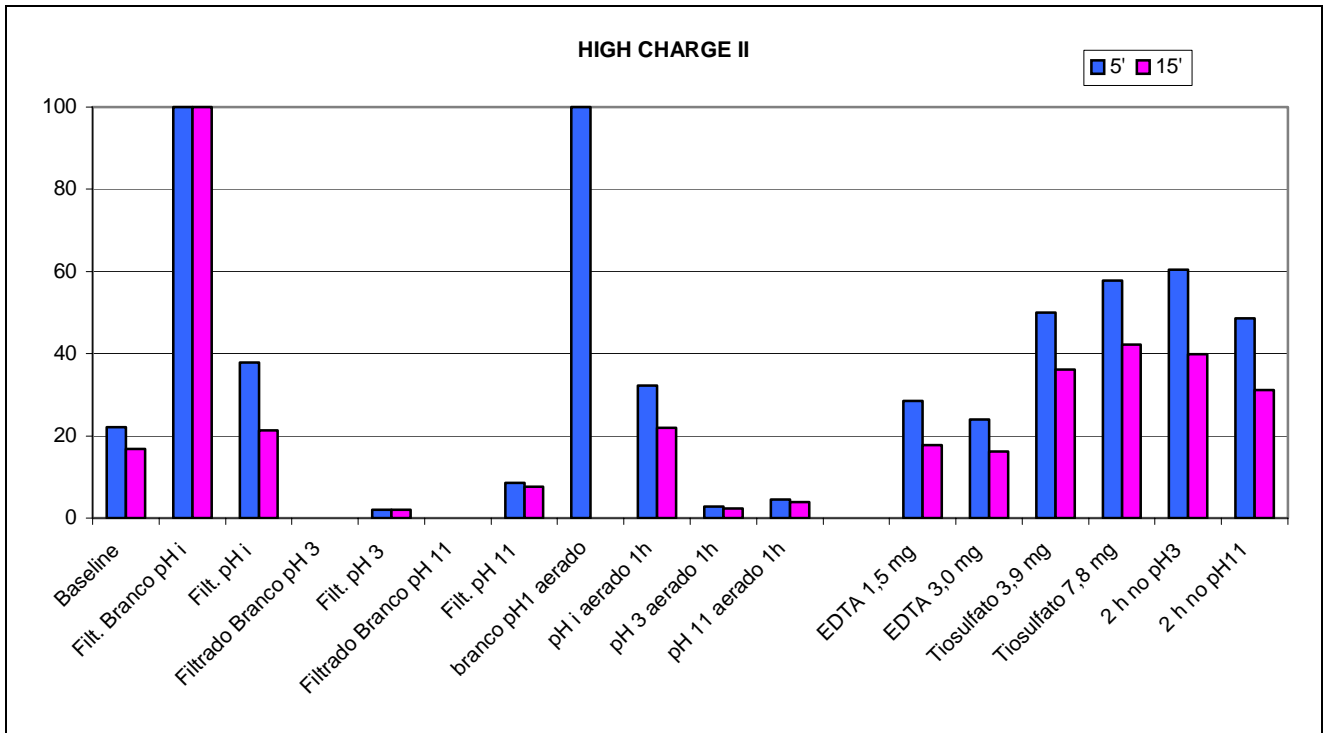


Figure 3 – Toxicity test results with the effluent High Charge II in August /2003.

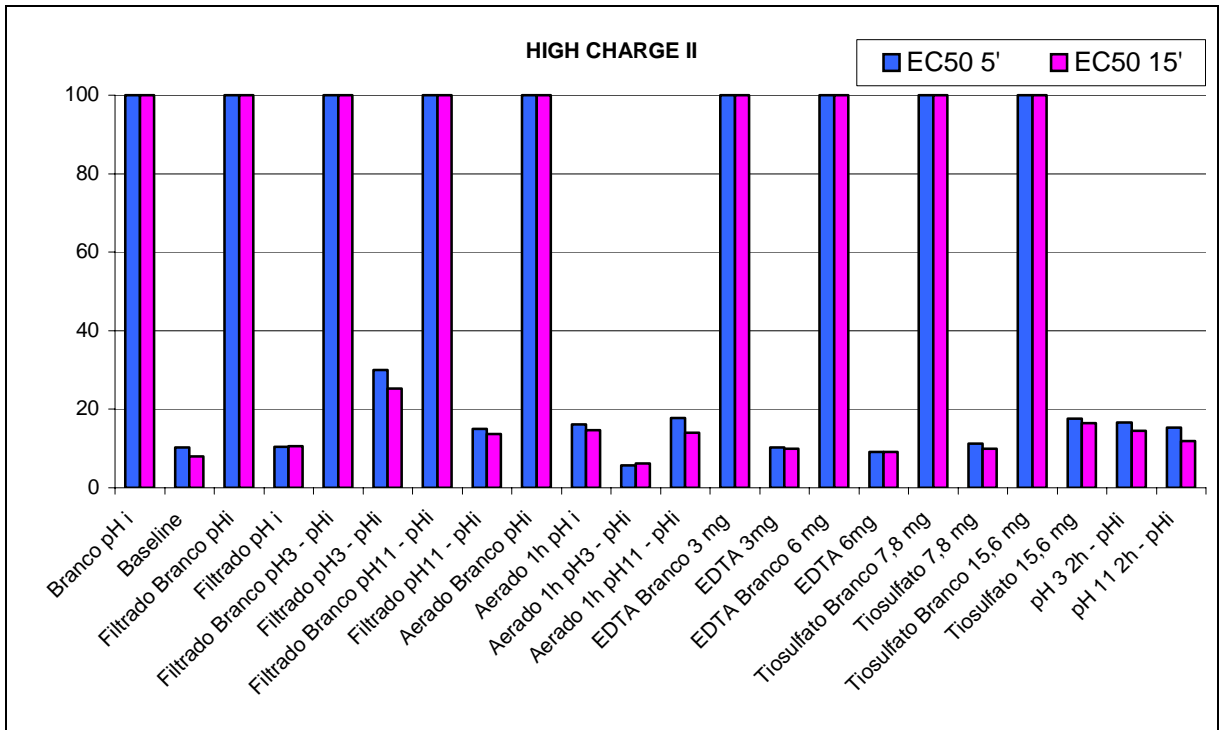


Figure 4- Toxicity test results with the effluent High Charge II in September /2003.

c) Acid Bleaching II

The TIE made either in August or in September of 2003 (Figures 5 and 6) showed that the toxicity in the effluent acid bleaching II may be reduced to half with tiosulphate addition, which eliminates the oxidants and, with the filtering of the effluent in neutral or alkaline pH, which shows that many contaminants are present in the solids, that are high in this effluent.

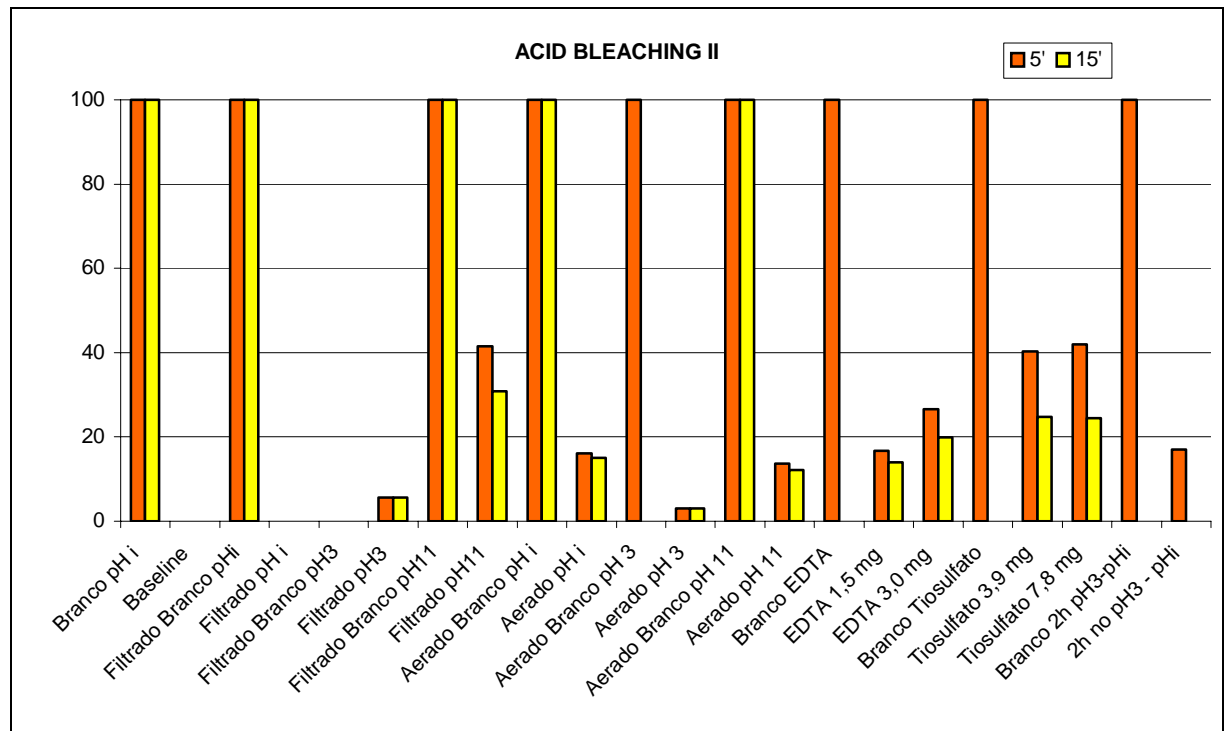


Figure 5 – Toxicity test results with the effluent Acid Bleaching II in August /2003.

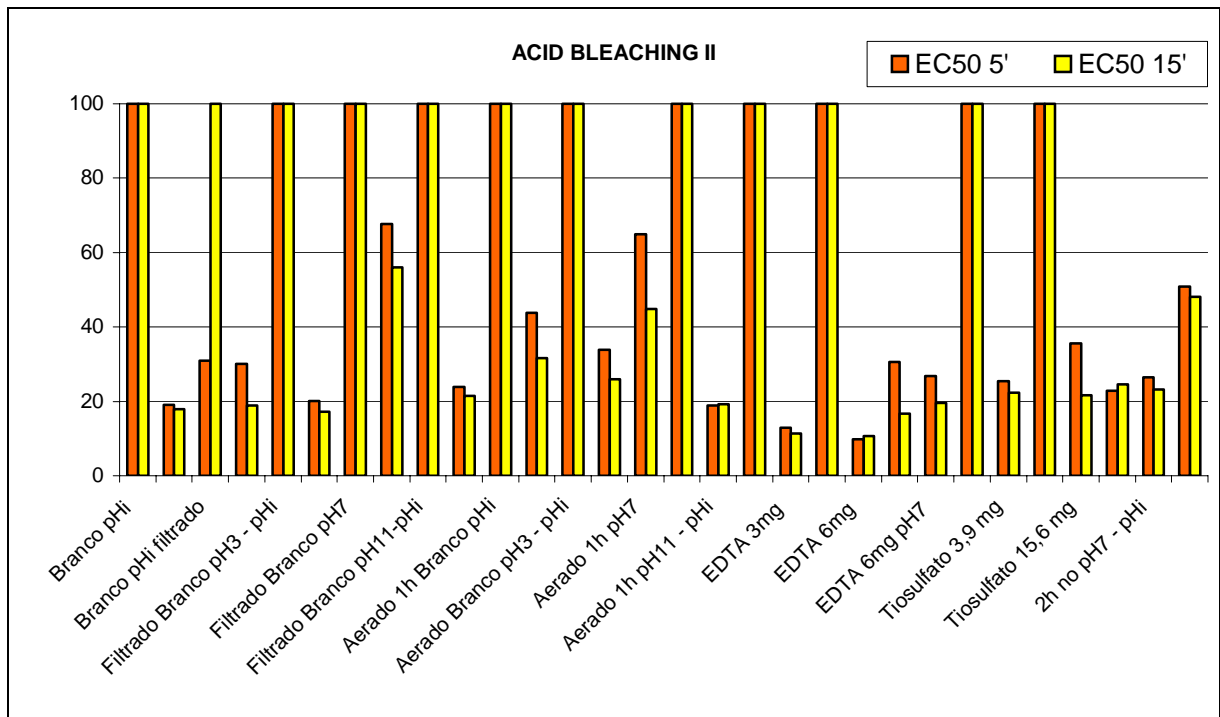


Figure 6 – Toxicity test results with the effluent Acid Bleaching II in September /2003.

d) Alkaline Bleaching II effluent

Almost all the manipulations made with the effluent alkaline bleaching II, which involved adjust of pH to neutral, reduced toxicity in the effluent (Figures 7 and 8). It is important to notice the filtering of the effluent, which reduced its toxicity, too, indicating that some toxic compounds are present in the solids in suspension, and also the addition of EDTA to the effluent, after its neutralization that reduced eight times the initial toxicity of the effluent alkaline bleaching II, indicating that there are metals and these were better treated at pH 7.

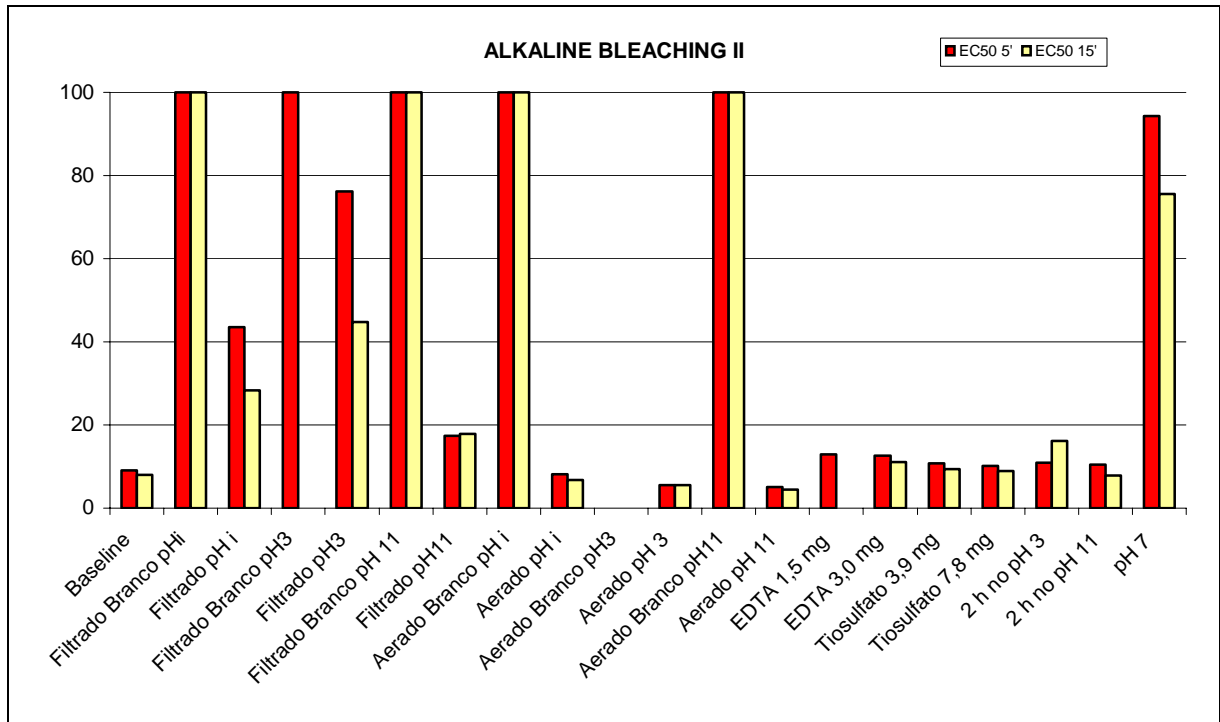


Figure 7 – Toxicity test results with the effluent Alkaline Bleaching II in August /2003.

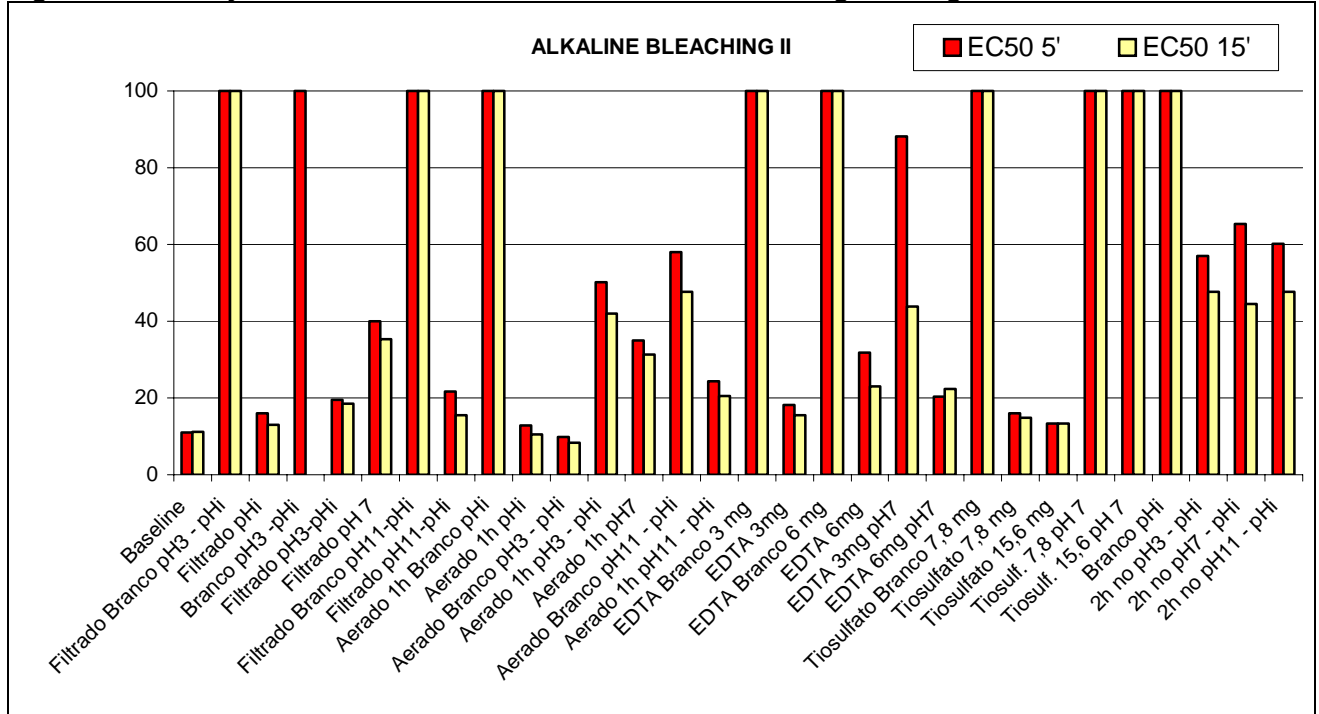


Figure 8– Toxicity test results with the effluent Alkaline Bleaching II in September / 2003.

e) *Evaporation 2*

The manipulations with the effluent Evaporation II reduced its toxicity in aeration at alkaline pH and also in neutral pH, showing that its toxicity is caused by volatile compounds, like TRS, for instance. The toxicity was not very reduced, the numbers fell to half (Figures 9 and 10). It is important to rebound that many of the natural compounds of wood, like fatty and resin acids are toxic to the organisms (Cherr et al, 1987) and they could be detected in the manipulation with C18 not made in this study because of a delay in the arrival of the C18 columns.

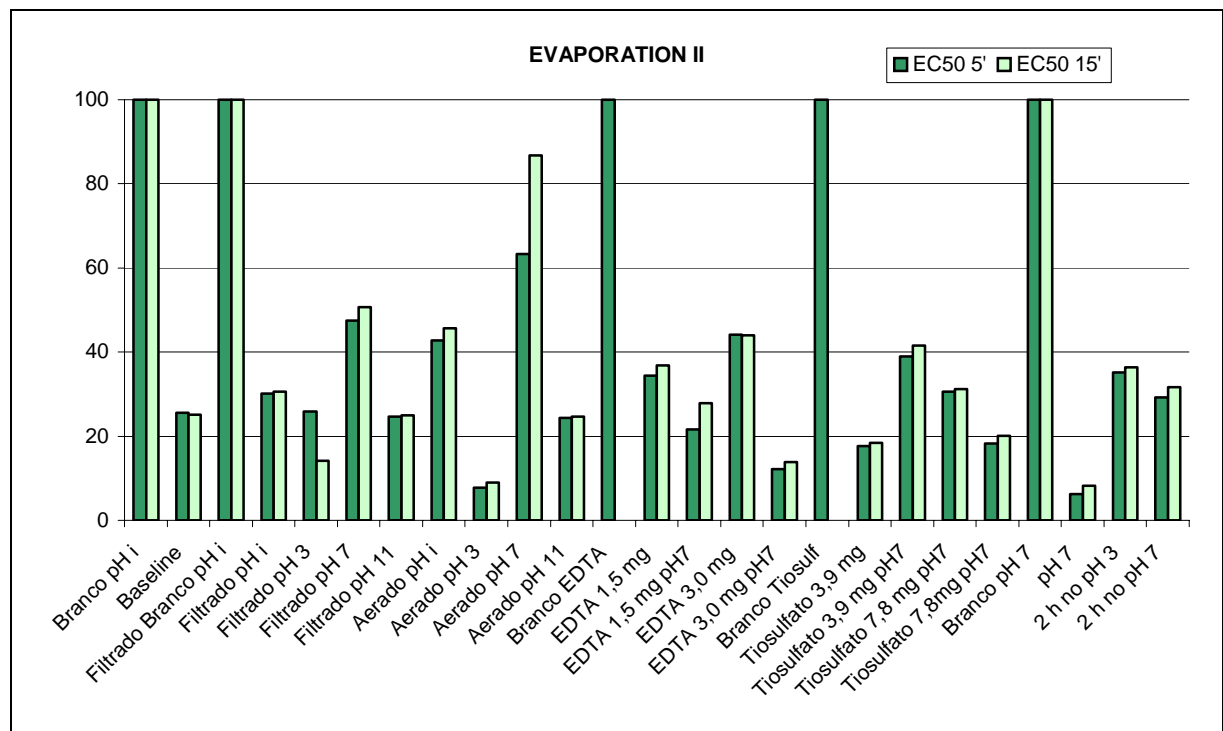


Figure 9 – Toxicity test results with the effluent Evaporation II in August /2003..

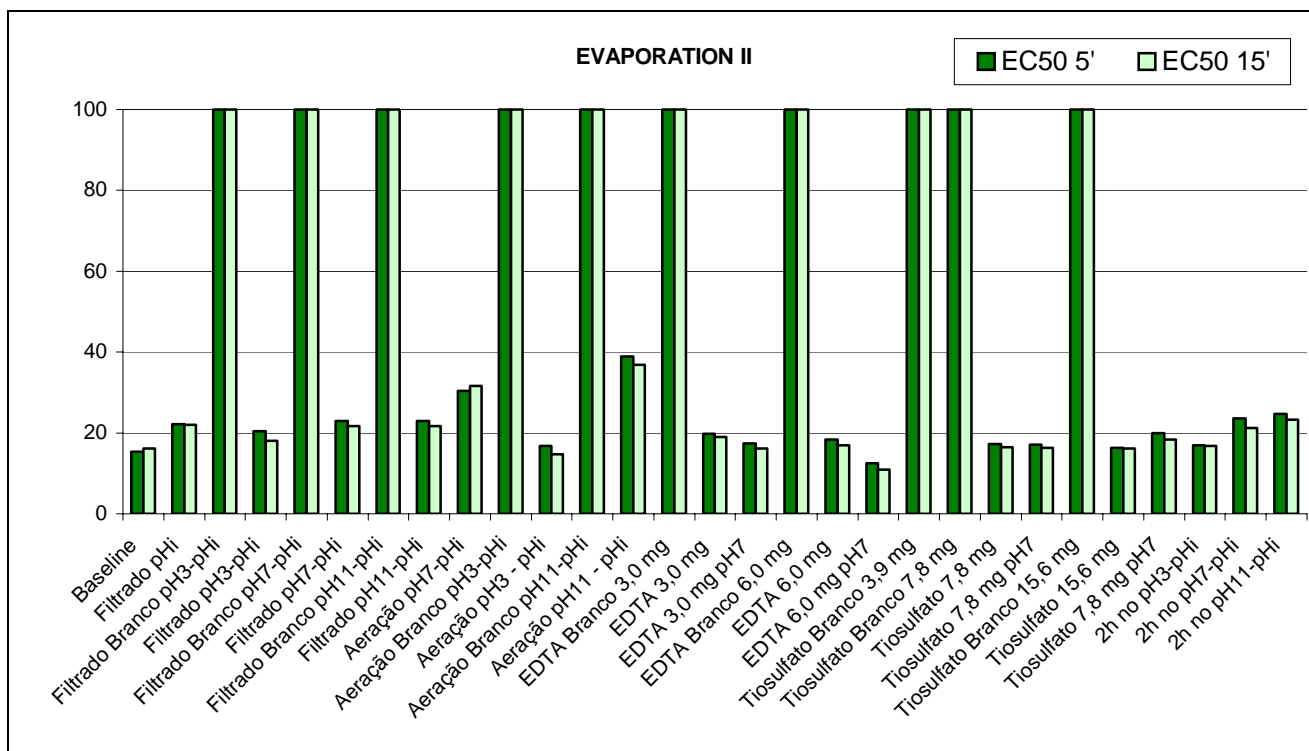


Figure 10 – Toxicity test results with the effluent Evaporation II in September /2003.

f) Bleaching 1

The toxicity in the effluent Bleaching I varied a lot in the two samplings and it seems to be linked to several compounds. Various manipulations reduced its toxicity, such as filtering, EDTA and tiosulphate addition and pH shock. These manipulations indicate that there are contaminants in the solids, metals and oxidants in the effluent. In the sampling of September, the toxicity of this effluent was also reduced with the aeration, indicating the presence of volatiles (Figures 11 and) or surfactants (Cook et al, 2003).

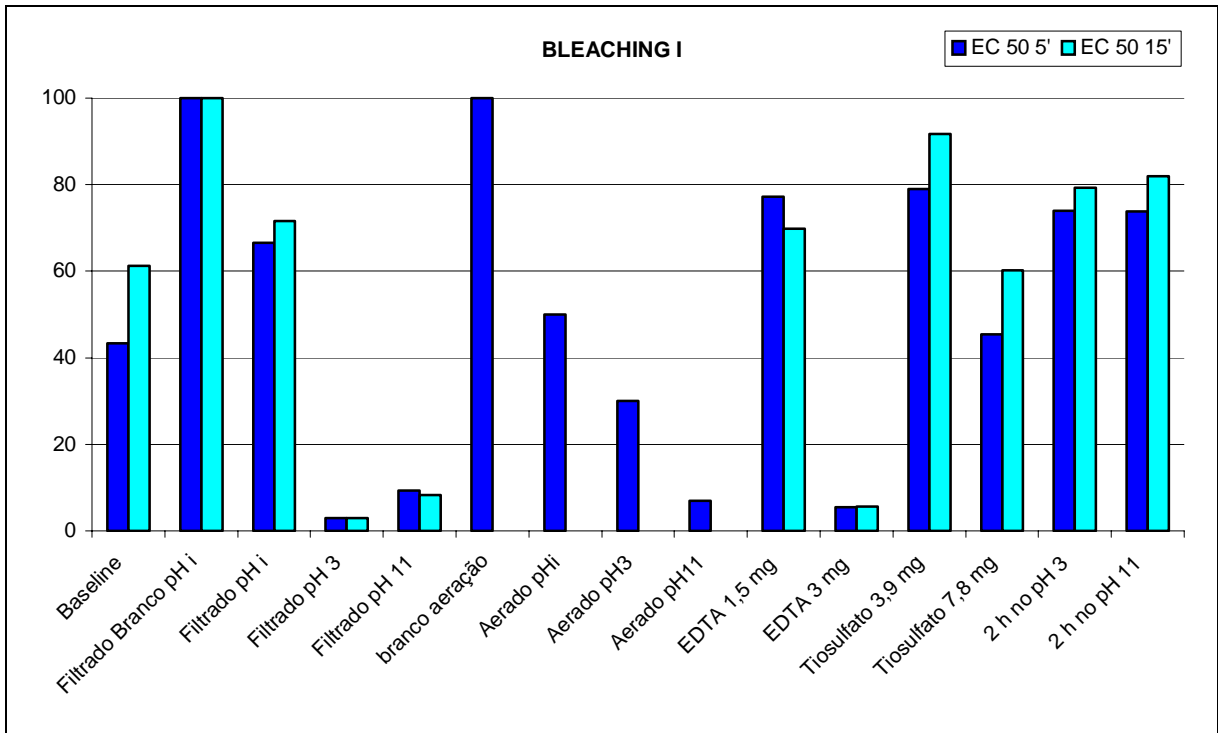


Figure 11 – Toxicity test results with the effluent Bleaching I in August /2003.

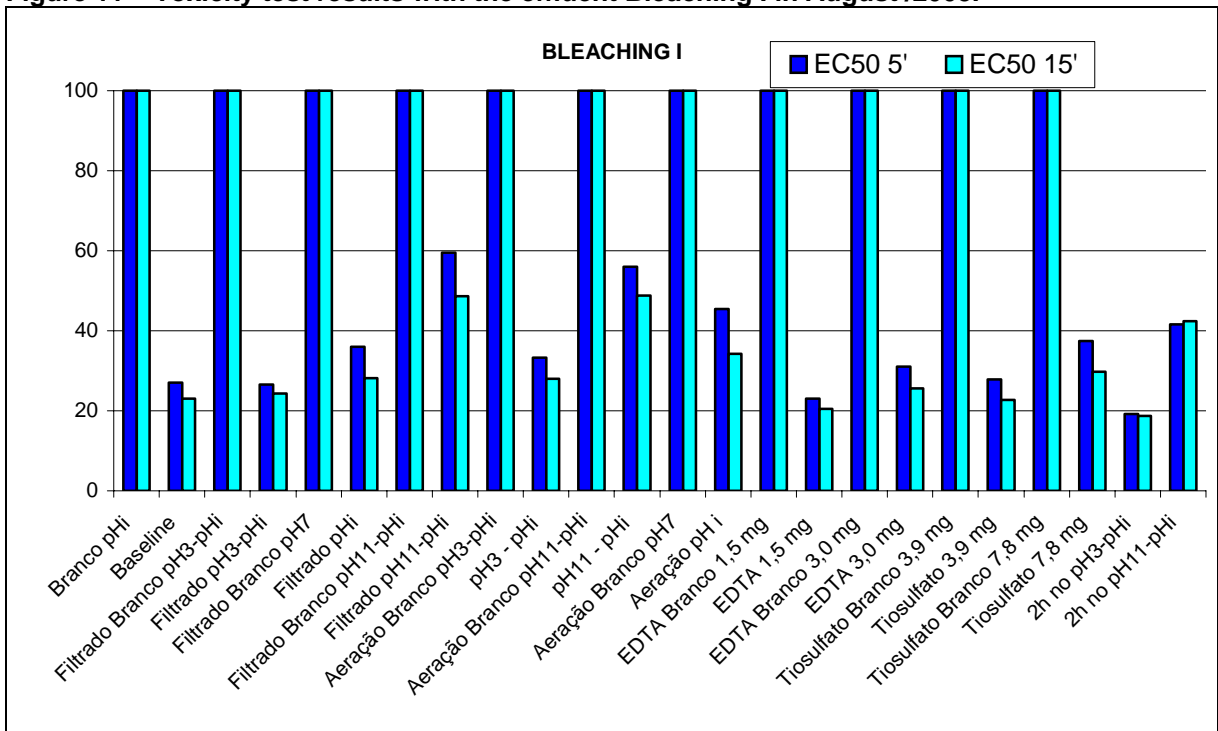


Figure 12 – Toxicity test results with the effluent Bleaching I in September /2003.

Many of the effluents above had different behavior, concerning the physical-chemical parameters, toxicity and response to TIE. Bailey et al (1995) also observed this difference at

the responses to TIE in the same effluent sampled in two different occasions, demonstrating the importance to sample at least three times.

CONCLUSIONS

The manipulations that best reduced acute toxicity of the High Charge effluent were the ones related to pH shock, preferably to alkaline. In slightly alkaline pH, through aeration or tiosulphate or EDTA addition it is possible to reduce the toxicity in this effluent to half. This effluent shock in pH 3 followed by filtering also reduces a lot its toxicity. There are several sources responsible for the toxicity of this effluent, such as: volatiles, metals, oxidants, compounds that run to acid pH and/or surfactants.

The effluent High Charge II had its toxicity highly varied. In both samplings, the manipulations that showed the best results were: tiosulphate addition (demonstrating oxidant presence) and pH shock for acid during two hours.

The toxicity in the effluent Acid Bleaching II is mainly due to oxidants, which are present in bigger concentration in this effluent, and the toxic compounds present in the solids.

Great part of the toxicity in the effluent Alkaline Bleaching II is reduced with the neutralization of the effluent. This effect is maximized when adding EDTA to the effluent in pH 7, and the toxicity was reduced in up to eight times.

Evaporation II toxicity is caused mainly by the TRS. The stripping of the effluent in alkaline pH or neutral reduces its toxicity to half.

The effluent Bleaching I has a very varying toxicity, and the cause for that also seems to be very varied. There is the most constant contribution of the solids, metals and toxic oxidants, besides volatile compounds present sporadically. Its treatment seems to be hard, because many conjugated manipulations of this effluent would be necessary to reduce its toxicity.

RECOMENDATIONS

Keep the pH of High Charge I the most alkaline possible and aerate it.

Reduce the pH of High Charge II and reduce the oxidants present in it.

Reduce the charge of oxidants and solids from the effluent Acid Bleaching II.

Neutralize the effluent Alkaline Bleaching II and add EDTA to the primary treatment at a 3mg/L concentration. This test must be repeated in laboratory for two more times before it is tested "in situ".

Strip the effluent Evaporation II.

Be especially careful with the effluent Bleaching I, once it is very toxic and hard to treat, because the sources seem to be varied. Initially, it is recommended to filter this effluent, have a pH shock and reduce the present oxidants. A 7,8mg/L concentration of tiosulphate would be interesting if it is added to this effluent.

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