FLOCCULATION/PRECIPITATION STUDIES WITH A BIOLOGICAL SECONDARY EFFLUENT FROM A BLEACHED KRAFT PULP MILL

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ABSTRACT

This paper describes some alternative procedures for the tertiary treatment of a secondary pulp mill effluent based upon the use of precipitants in combination with the addition of activated carbon or some mill solid residues (dregs, grits, coal boiler bottom ash). The effluent samples were taken after the clarifier that closes an UNOX activated sludge secondary biological treatment in a Brazilian kraft pulp mill. The samples were characterized by their physical chemical features such as apparent color, AOX and trace elements (Cu, Zn, Pb and Cd). Afterwards, they were submitted to laboratory precipitations with two types of precipitants (aluminum sulfate or ferric chloride). Alternatively, the precipitants were combined with dregs, grits, coal boiler bottom ash or activated carbon. These treatments were able to provide noticeable reductions on apparent color, specially the utilization of aluminum sulfate alone or in combination with activated carbon. Considering the concentration of organo-halogenated compounds (AOX), the major reduction was observed with the addition of ferric chloride and activated carbon. All trace elements were reduced in concentration when ferric chloride plus solid residues were used in the flocculation stage. The combination of precipitants and kraft mill solid residues may lead to significant savings on the use of the precipitants.

INTRODUCTION

The pulp industry is in a continuous search for environmental improvements. Wastewater quality and quantity are key issues. The stricter legislation, the possible obligation to pay to the use and to discard the water, and the upgraded environmental awareness in the corporations, are the main reasons for this trend.

End-of-pipe techniques, associated with pollution prevention and cleaner production methods are becoming the dominant measures being adopted by the industry. Although pollution prevention and eco-efficiency have the advantage to reduce the generation of wastes, there are many situations where the better solution is an efficient end-of-pipe technique.

Wastewater treatment plants are being upgraded to result in effluents that could be recycled internally or do not cause harmful effects in the receiving water streams.

Flocculation/precipitation is an excellent way to improve water quality. Both color and COD may be dramatically improved by this treatment. The most commonly used precipitants are alum (aluminum sulfate) and ferric chloride. They may be used alone or in combination with some coadjutors (polymers, activated carbon, etc.).

The possibility of utilizing mill solid residues such as dregs, grits and coal-fired boiler bottom ash in effluent treatment (9) represents an attractive alternative for the internal reuse of these residues generated by the pulp industry. The use of activated carbon as a flocculating coadjutor in systems for industrial effluent treatment is a well-known procedure (3) (11) (12). The generation of toxic halogenated organic compounds (AOX) in some bleached kraft pulp mills has been widely studied. AOX is understood to be generated by the use of chlorine, hypochlorite and chlorine dioxide in the pulp bleaching. These oxidants, when in contact with lignin, react with these organic molecules, forming organo-halogenated compounds. In case AOX is not controlled and kept in high concentrations, they may contaminate the organisms of he food chain or to accumulate in sediments (6) (7) (8).

In other hand, trace elements of environmental relevance in anthropogenetic processes may go through different stages of enrichment and bio-magnification. After some time, they may be mobilized or released into the environment, resulting in harmful effects. Thus, it is always important to be aware of the concentration of these elements in the labile fractions that may be disposed into the aquatic medium in general (13).

MATERIAL AND METHODS

The investigation was performed in three stages: a) general characterization of the effluent (determination of apparent color, AOX concentration and trace element levels (Cu, Zn, Pb and Cd)); b) treatment with precipitants [$Al_2(SO_4)_3$ and $FeCl_3$ (4)] and adsorbents [dregs, grits, coal boiler bottom ash and activated carbon #1 (analytical grade) and #2 (commercial grade); and ; c) effluent characterization after treatment (determination of apparent color, AOX and trace elements).

Dregs and grits are solid residues generated during the kraft recovery process. Bottom ash comes from the coal boiler as the residue of the burnt mineral coal in the power house.

TREATMENTS

The treatments applied to the effluent consisted of 12 precipitants/flocculants and adsorbents combinations: $FeCl_3$ without any adsorbent, $FeCl_3$ and grits, $FeCl_3$ and dregs, $FeCl_3$ and bottom ash, $FeCl_3$ and activated carbon #1, $FeCl_3$ and activated carbon #2, $Al_2(SO_4)_3$ without any adsorbent, $Al_2(SO_4)_3$ and grits, $Al_2(SO_4)_3$ and dregs, $Al_2(SO_4)_3$ and bottom ash, $Al_2(SO_4)_3$ and activated carbon #1, and $Al_2(SO_4)_3$ and activated carbon #2. This step was carried out with the use of a jar test using the adsorbent, the sample and the precipitant/flocculant. The pH was corrected to 4.7 for $Al_2(SO_4)_3$ and to 4.0 for $FeCl_3$. The mixture was shaken in a mechanical shaker at high speed for 1 minute and at low speed for 15 minutes and then left to stand for 30 minutes, to allow the precipitation of the flocs.The apparent color, the AOX content and the concentration of trace elements (Cu, Zn, Pb and Cd) were determined in the collected samples of treated effluent.

RESULTS AND DISCUSSIONS

Apparent color

Table 1. Summarized statistics of the behavior of effluent apparent color as a function of the values obtained for the samples submitted to the various tertiary treatments.

Statistical Parameter	**Apparent Color** (mg Pt . Co/L)
Average	84.73
Standard deviation	28.69
Coefficient of variation (%)	33.85

*Number of observations = 258

Table 2. Relative distribution and ranking of the samples classified according to the type of flocculant as a function of apparent color.

Classification (%)	**$Al_2(SO_4)_3$**	**$FeCl_3$**
• Proportion of samples classified in the group of highest apparent color	16.67	34.29
• Proportion of samples classified in the group of lowest apparent color	83.33	65.71
Total	100 %	100 %

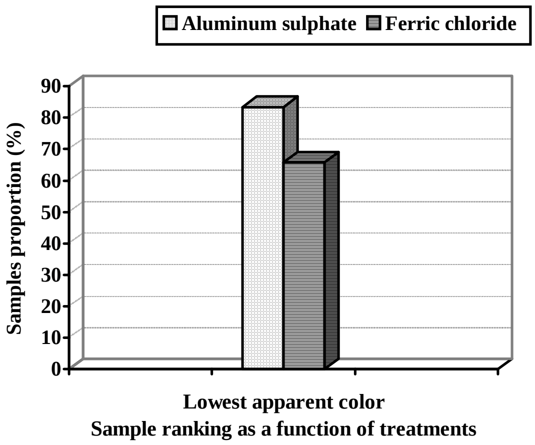

Figure 1. Relative distribution of the number of samples classified according to the type of flocculants for the apparent color.

Table 2 shows that aluminum sulfate was the flocculant that yielded the best results for the reduction of apparent color. The aluminum sulfate charge of 400 mg/L gave the largest number of samples with lowest apparent color values , being considered the most effective charge added.

All adsorbents can be used since no differences were observed between the various treatments, except for grits. Economically, the use of solid residues produced by the industry (dregs and bottom ash) is more attractive at the highest charged concentrations used (82.4 and 105.0 mg/L, respectively).

Organo-halogenated compounds (AOX)

Table 3. Summarized statistics of AOX behavior as a function of treatments

Statistical parameter	**AOX (mg/L)**
Average	0.99
Standard deviation	0.36
Coefficient of variation (%)	36.36

*Number of observations = 88.

Table 4. Relative distribution of samples classified according to the flocculant and to AOX concentration

Classification (%)	**$Al_2(SO_4)_3$**	**$FeCl_3$**
• Number of samples classified in the group of highest AOX concentration	45.30	11.43
• Number of samples classified in the group of lowest AOX concentration	54.70	88.57
Total	100 %	100 %

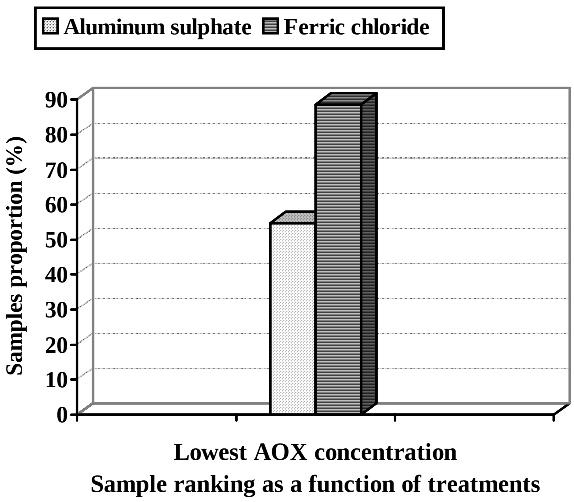

Figure 2. Relative distribution of samples classified according to the type of flocculants and for the AOX concentration.

Table 4 shows that the coagulant that yielded the best results was ferric chloride, with 88.57% of the samples being classified as those presenting the lowest AOX concentration.
The industry is obviously interested in recycling its solid residues. In addition, the various statistical procedures employed showed that there was no significant differences among the various types of adsorbents, except for activated carbon #2 and grits, which presented a larger number of samples with lower AOX levels.
The charged concentrations of active carbon #2 tested (100, 150 and 200 m/L) also showed no significant differences , and the same applied to grits charged concentrations (58.2 and 78.3 m/L). For this reason , the lowest charges, the best for economical savings.

Trace elements (TE)

Table 5. Average results obtained n the analysis of trace elements.

Treatment	Trace elements (mg/L)			
	Zn	Cu	Pb	Cd
Characterization (untreated effluent)	1.170	0.246	0.123	0.006
Aluminum sulfate	1.050	0.073	0.018	0.002
Aluminum sulfate + dregs	1.768	0.158	0.014	0.002
Aluminum sulfate + activated carbon #1	0.886	0.103	0.016	0.003
Aluminum sulfate + activated carbon #2	0.727	0.038	0.028	0.002
Aluminum sulfate + grits	1.958	0.028	0.017	0.002
Aluminum sulfate + bottom ash	1.743	0.056	0.020	0.001
Ferric chloride	0.870	0.040	0.012	0.002
Ferric chloride + dregs	0.624	0.040	0.005	0.002
Ferric chloride + activated carbon #1	1.174	0.057	0.012	0.001
Ferric chloride + activated carbon #2	0.988	0.087	0.007	0.001
Ferric chloride + grits	0.985	0.034	0.012	0.001
Ferric chloride + bottom ash	0.796	0.029	0.016	0.002

Analysis of the results in Table 5 shows that during the untreated effluent characterization process, an average Zn concentration of 1.170 mg/L was obtained. The treatment that yielded the lowest Zn concentration was the combination of ferric chloride and dregs with a low variation corresponding to approximately 4.33% of the average concentration. A similar analysis can be done for the remaining data. It was clear that ferric chloride alone or combined with dregs, grits or bottom ash had excellent behavior to reduce trace elements.

CONCLUSIONS

In all alternative treatments applied to the secondary effluent of a bleached kraft pulp mill there were appreciable reductions of apparent color, AOX concentration and trace elements levels. Aluminum sulfate (400 mg/L dosage) was more effective in color reduction. The use of ferric chloride (250 mg/L dosage) as a flocculant/precipitant may represent an important saving factor in view of the possibility of its low-cost production from process chemicals (chlorine and hydrochloric acid) and from iron residues. By combining its use with the use of residual coadjutors (dregs, grits and bottom ash), good results can be obtained, as demonstrated here, with interesting savings of chemical raw materials. At the same time, the solid residues are converted into reused chemicals in the process. However, eco-toxicological studies with bio-essays are recommended prior to the use of these residues , in order to better understand their side environmental impacts.