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ALTERNATIVE PROCEDURES FOR THE TREATMENT OF EFFLUENTS OF BLEACHED KRAFT CELLULOSE INDUSTRY

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This work describes alternative procedures for the treatment of secondary effluent from the pulp industry using solid residues of the process (dreg, grit, heavy ash), and active carbon. The effluent samples were characterized in terms of color, content of halogenated compounds and trace elements, and then submitted to a coagulation step with ferric chloride and aluminium sulphate as coagulants/flocculants, coadjuvated by dreg, grit, heavy ash and active carbon. An appreciable reduction of color and halogenated compound content of the final effluent was observed, as well as a significant saving on flocculants.

KEY WORDS: Kraft process, pulp bleaching cellulose industry

INTRODUCTION

The possibility of utilizing solid residues such as dreg, grit and heavy ash in effluent treatment[9] and in ferric chloride production represents an attractive alternative for the recycling of refuse in the cellulose and pulp industry. The use of active carbon as a flocculating coadjuvant in systems of industrial effluent treatment is a well known procedure[3,11,12].

Concern about the concentration of organohalogen compounds in industrial Kraft cellulose effluents is justified by the use of chloride and chloride dioxide in one of the steps of the standard pulp bleaching procedure[14,17]. These products, when in contact with lignin, in addition to coloring the water, generate organohalogen compounds that, if uncontrolled, may contaminate all the organisms of the food chain[6,7,8]. In turn, trace elements of environmental relevance in anthropogenic processes may go through

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different stages of enrichment and biomagnification and, after some time, may be mobilized into the environment. 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 conducted in three stages: (a) general characterization of the effluent: determination of apparent color, AOX concentration and trace element (Cu, Zn, Pb and Cd) levels; (b) treatment with coagulants[4] [$Al_2(SO_4)_3$ and $FeCl_3$] and adsorbents [dreg, grit, heavy ash and active carbon 1 (p.a.) and 2 (technical grade)]; and (c) effluent characterization after treatment (determination of apparent color, AOX and trace elements).

Dreg and grit are solid residues generated during the recovery phase of the boiling liquor in the production of sulfate pulp. Heavy ash comes from the boiler furnace as the residue of mineral coal burning in the power unit of the industry.

Sampling

Effluent samples that had not received any type of coagulant were collected from the overflow of the secondary treatment in a bleached kraft cellulose industry. The samples were placed in glass containers for the measurement of AOX (combined organohalogen compounds) and in polyethylene flasks for the determination of apparent color and trace elements. The containers were properly labeled and stored in a cold room[1,10].

Analytical Methods

Apparent color was measured by a photometric method using a Micronal 3295 instrument at a wavelength of 440 nm; the analytical curve was obtained with a standard platinum-cobalt chloride solution[2].

Total organohalogen compounds (AOX) were determined with a Euroglas ECS 1000 adsorption instrument[10,16].

Trace elements (TE) were measured by atomic absorption spectrophotometry[15] using a Perkin Elmer model 3030 instrument equipped with an HGA-400 graphite oven, an AS-40 automatic sampler and a PR-100 printer. The technique of successive standard addition was used for all elements analyzed and a certified NIST standard (Estuarine Sediment Nr. 1646) was used for solid residues[5]. The treatments applied to the effluent consisted of 12 coagulant/flocculant and adsorbent combinations: $FeCl_3$ without an adsorbent, $FeCl_3$ and grit, $FeCl_3$ and dreg, $FeCl_3$ and heavy ash, $FeCl_3$ and active carbon 1, $FeCl_3$ and active carbon 2, $Al_2(SO_4)_3$ without an adsorbent, $Al_2(SO_4)_3$ and grit, $Al_2(SO_4)_3$ and dreg, $Al_2(SO_4)_3$ and heavy ash, $Al_2(SO_4)_3$ and active carbon 1, and $Al_2(SO_4)_3$ and active carbon 2. This step was carried out with the aid of a Jar test using the adsorbent, the sample and the coagulant, and the pH was corrected to 4.7 for $Al_2(SO_4)_3$ and to 4.0 for $FeCl_3$. The preparation 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.

The apparent color, the AOX content and the concentration of trace elements (Cu, Zn, Pb and Cd) were determined in the resulting supernatant.

RESULTS AND DISCUSSION

Apparent color

The mean apparent color of the effluent before treatment was 1081.4 mg Pt Co/L. Low color values characterize treatments considered to be the best[6]. For this reason, only the data related to the treatment groups showing to the lowest color values (mg Pt. Co/L) will be reported here.

Table 1 shows a statistical description of the behavior of apparent effluent color after treatment with coagulants/flocculants and adsorbents.

A value of 12.54, without Yates correction, was obtained in the classification test (highest and lowest apparent color) versus the flocculant (aluminum sulfate and ferric chloride). The classification was found to be associated with the type of flocculant employed. In other words, the proportion of samples treated with aluminum sulfate, classified has having the lowest apparent color, was significantly different from the proportion of samples treated with ferric chloride. Figure 1 and Table 2 illustrate the relative distribution of the samples.

The same structure for data presentation was used for the different coagulant concentrations and for the different types of adsorbents and their respective concentrations.

Table 2 shows that aluminum sulfate was the coagulant that yielded the best results for the reduction of apparent color, with 83.33% of the samples having the lowest values of apparent color. The aluminum sulfate concentration of 400 mg/L gave the largest number of samples with lowest apparent color values.

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

Statistical Parameter	*Apparent Color (mg Pt · Co/L)*
Mean apparent color	84.73
Standard deviation	28.69
Coefficient of variation (%)	33.85

* Number of observations = 258

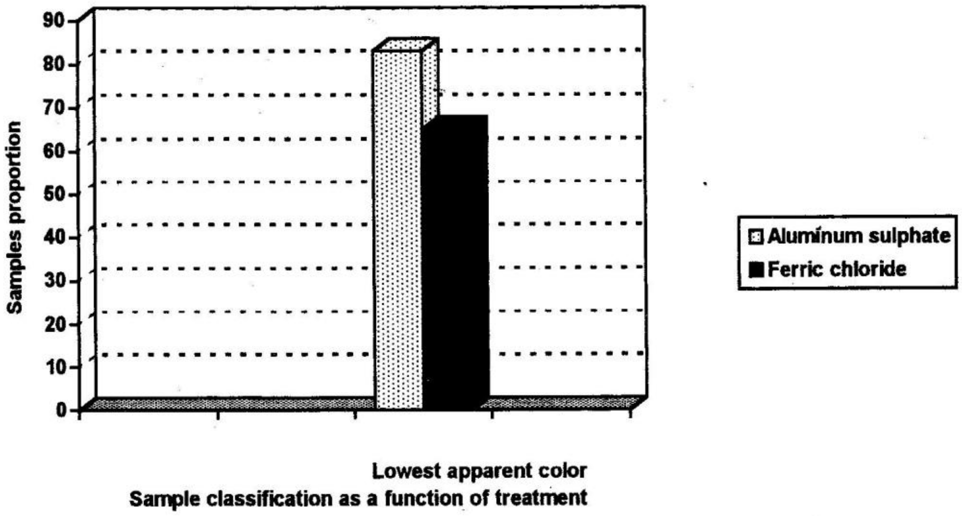

Figure 1 Relative distribution of the number of samples classified as a function of the flocculants and of the classification of apparent color (mg Pt Co/L).

Table 2 Relative distribution of the samples classified according to the type of flocculant and sample classification as a function of apparent color (mg Pt Co/L)

Classification	$Al_2(SO_4)_3$	$FeCl_3$
Proportion of samples classified into the group of highest apparent color	16.67	34.29
Proportion of samples classified into the group of lowest apparent color	83.33	65.71
Total	100.00	100.00

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

Organohalogen compounds (AOX)

Mean AOX concentration in the untreated effluent was 3.55 mg/L. Table 3 presents the behavior of the effluent with respect to the AOX parameter when the data were submitted to the Kruskal-Wallis test (group presenting the lowest mean AOX value), in relation to the treatment used.

Table 3 Summarized statistics of AOX behavior as a function of treatment

Statistical parameter	*AOX (mg/L)*
Mean AOX content	0.99
Standard deviation	0.36
Coefficientof variation (%)	36.36

* Number of observations = 88

Table 4 shows the percentage of samples classified as having the lowest and highest AOX concentrations and Figure 2 illustrates the percentage of samples with the lowest AOX concentration.

Table 4 shows that the coagulant that yielded the best result 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 difference among the various types of adsorbents, except for active carbon 2 and grit, which presented a larger number of samples with lower AOX levels.

The concentrations of active carbon 2 tested (100, 150 and 200 mg/L) also showed no significant differences and the same applied to grit concentrations (58.2 and 78.3 mg/L).

Trace elements (TE)

Mean TE concentrations for the untreated effluent were 1.170 mg/L for Zn, 0.246 mg/L for Cu, 0.123 mg/L for Pb and 0.006 mg/L for Cd.

Table 5 lists the mean results obtained in the determination of zinc, copper, lead, and cadmium.

Table 4 Relative distribution of samples classified according to the flocculant and to AOX concentration (mg/L)

Classification	$Al_2(SO_4)_3$	$FeCl_3$
Number of samples classified into the group of highest AOX concentration	45.30	11.43
Number of samples classified into the group of lowest AOX	54.70	88.57
Total	100.00	100.00

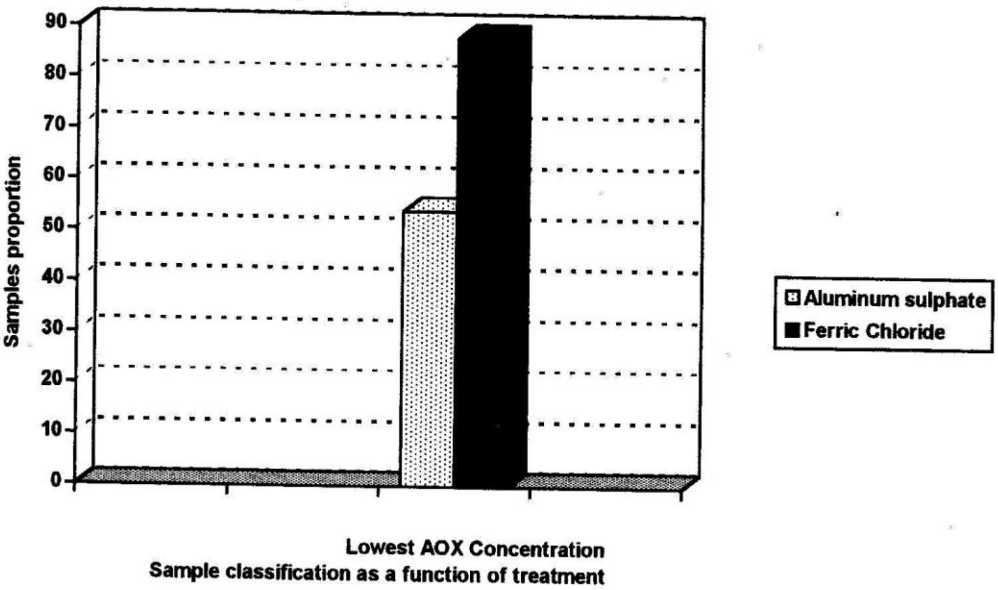

Figure 2 Relative distribution of samples classified according to the coagulants/flocculants and AOX concentration (mg/L).

Table 5 Mean results obtained in 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 sulphate	1.050	0.073	0.018	0.002
Aluminum sulphate + dreg	1.768	0.158	0.014	0.002
Aluminum sulphate + active carbon 1	0.886	0.103	0.016	0.003
Aluminum sulphate + active carbon 2	0.727	0.038	0.028	0.002
Aluminum sulphate + grit	1.958	0.028	0.017	0.002
Aluminum sulphate + heavy ash	1.743	0.056	0.020	0.001
Ferric chloride	0.870	0.040	0.012	0.002
Ferric chloride + dreg	0.624	0.040	0.005	0.002
Ferric chloride + active carbon 1	1.174	0.057	0.012	0.001
Ferric chloride + active carbon 2	0.988	0.087	0.007	0.001
Ferric chloride + grit	0.985	0.034	0.012	0.001
Ferric chloride + heavy ash	0.796	0.029	0.016	0.002

Analysis of the results in Table 5 shows that during the characterization process a mean Zn concentration of 1.170 mg/L zinc was obtained. The treatment that yielded the lowest mean Zn concentration was the combination of ferric chloride and dreg, with a low dispersal corresponding to approximately 4.33% of the mean concentration. A similar analysis can be done for the remaining data.

CONCLUSIONS

In all alternative treatments applied to the secondary effluent of the bleached Kraft cellulose industry there was an appreciable reduction of apparent color, of AOX concentration and of TE levels. The use of ferric chloride as a coagulant/flocculant may represent an appreciable economic factor in view of the possibility of its low-cost production from process residues (chloride/hydrochloric acid) and from iron ore residues. By combining its use with the use of residual coadjuvants (dreg, grit and heavy ash), good results can be obtained, as demonstrated here, with savings of supplies.

References

1. E. G. Agudo, *Guia de coleta e preservação de amostras de água*. São Paulo: CETESB, 150 p (1987).
2. APHA AWWA. *Standard methods for the examination of water and watstewater*. Whashington, 1268 p (1985).
3. AWWA Standards For Granular Activated Carbon. *Journal American Water Works Association*, Washington, **66**, 672–681 (1974).
4. J. R. Azevedo Neto, J. Povineli, A. C. Parltore, I. Hespanol, A. C. Rossin and S. Yaguinuma, *Técnica de abastecimento e tratamento de água*. São Paulo: CETESB, **2**, 951 p (1976).
5. M. Bettinelli, V. Pastorelli and U. Baroni, STPF Determination of trace metals in fly ash samples. *Atomic spectroscopy*, Italia, **7**, 45–48 (1986).
6. N. R. Blake and J. L. Zuncich, Reduction of chlorinated organic in pulp and paper mill effluent. In: Environmental Conference, Atlanta. *Anais*... Atlanta: Tappi Press, **1**, p. 445–451 (1991).
7. C. W. Bryant, J. W. Dettmer and W. A. Barkley, Removal of organic chlorine and color from kraft wastewater and lagoon sludge underalternate treatment conditions. In: Environmental Conference, Atlanta. *Anais*... Atlanta: Tappi press, **2**, p. 807–812 (1991).
8. M. F. Celeste and O. Cáceres, Residuos de praguicidas clorados na represa do Ribeirão do Lobo (Broa) e nos seus rios tributários. *Ciência e Cultura*, São Paulo, **39**, 66–70 (1991).
9. J. T. Cookson, Adsorption mechanisms: the chemistry of organic adsorption on activated carbon. In: Cheremisinoff, P. N.; Ellebush, F. *Carbon adsorption handbook*. Ann Arbor: p. 241–279 (1980).
10. DIN. *Determination of adsorbable organically bonded halogens* (AOX): Germany, DIN 38409. Germany, part 14 (1985).
11. C. Froehlich, *Melhoramento de Efluentes da Indústria de Cellulose e Papel por carvão biológico*. Dissertação (Mestrado em Engenharia). Porto Alegre: UFRGS, Brasil, (1987).
12. G. Grulich, D. G. Hutton, F. L. Robertaccio and H. L. Glotzer, Treatment of organic chemicals plant wastewater with the Dupontpact process. *Alche Symposium Series*, New York, **69**, 127–134 (1973).
13. W. M. Hinds and W. K. Jackson, Eletrothermal atomisation atomic - absorption spectometry with the direct introduction of slurries. Determination of trace metals in soil. *Analyst*, **110**, 947–950 (1985).
14. N. Marwah, T. W. Joyce, C. L. Chen and J. S. Gratzl, A simple process modification to reduce chloro-organic (AOX) formation in the bleachplant. In: Environmental Conference, Atlanta. *Anais*... Atlanta: Tappi Press, **2**, p. 1029–1031 (1991).
15. SCAN. *Effluents from pulp mills:* organically bound chlorine by the AOX method. Denmark, SCAN-W **9**, 89 (1989).
16. H. U. Süss, N. Nummerfroh, L. W. Eul and J. Meir, Environmental aspects of shortsequence bleaching. Bleaching: *A Tappi Press*, Atlanta: Jamell, Hasan. p. 482–492 (1991).