Wat. Sci. Tech. Vol. 20, No. 1, pp. 149–160, 1988.
Printed in Great Britain. All rights reserved.

0273–1223/88 $0·00 + ·50

TREATABILITY STUDIES AND TOXICITY REDUCTION IN PULP AND PAPER MILL EFFLUENTS

J. B. Galvão F°*, V. M. Grieco*, R. P. A. Araújo**,
M. R. Ortolano*, E. Bertoletti** and M. L. L. C. Ramos*

**RIPASA S/A — Celulose e Papel, Largo São Bento 64, 16° andar,*
CEP 01029, São Paulo, SP, Brazil
***CETESB — Companhia de Tecnologia de Saneamento Ambiental,*
Av. Prof. Frederico Hermann Jr 345, CEP 05459, São Paulo, SP, Brazil

ABSTRACT

A study of the liquid effluents of various production process stages and of the final effluent of the RIPASA S/A Celulose e Papel plant, by means of conventional parameters and toxicity, was undertaken. Using these parameters, the performances of the current treatment system (an aerated pond) and of pilot-scale experimental systems (using aerobic biological processes with one or two stages) were compared. The two-stage system yields better results in the improvement of final effluent quality. Biological degradation rates were also determined. It is thought that these discharges will not have an impact on the receiving water, as far as toxicity is concerned.

KEYWORDS

Pulp and paper mill; industrial effluents; treatability; biological treatment; biological degradation rate; acute and chronic toxicity; fish; Ceriodaphnia; Daphnia; impact estimates.

INTRODUCTION

The pollution caused by pulp and paper mill liquid discharges represents a major problem. Few other industries have such high water requirements for their manufacturing process. On average, the volume discharged is between 80 and 150 m^3 per ton of finished product. This wastewater is discharged into rivers, lakes, and seas, and if it does not receive proper treatment it may be an environmental hazard to such ecosystems. Even though the effluents from this industry are composed of complex substances, the methods adopted for their treatment are based on conventional systems, i.e., physical or physico-chemical treatment and biological treatment. The design of treatment systems should be based on reduced scale studies for the proper assessment of the chosen system and selection of design parameters.

More recently, in addition to concerns regarding removal of organic matter, suspended solids, etc., other parameters have also been studied concerning the choice and operation of treatment systems. Particular attention has been given to the acute and chronic toxic effects which the components remaining in the final effluent may cause in receiving waters. RIPASA, one of the largest pulp and paper companies using the sulfate process (kraft) in the State of São Paulo, has been attempting to find specific solutions to reduce the impact of its effluents on receiving waters. To this end, to reduce the organic load of the final effluent, it has installed an energy recovery and effluent recycling system called the 'Lockman System', which has entailed, in addition to the control of gaseous effluents, a significant reduction in the volume of liquid effluents, due to the elimination of effluents generated by the scrubbing of gases which are flared off, which contain high levels of sulfur compounds.

The aim of this work was to investigate, on a pilot scale, the treatability of pulp and paper effluents, including the kinetic behavior of the aerobic process, and the reduction of effluent toxicity levels, and to assess the impact of the final effluents on the aquatic biological communities. In addition to the pilot-scale studies, the toxicity levels and main attributes of the different discharges generated by the production process were also investigated. These studies were the basis for the choice of a new treatment system to be implemented by RIPASA, replacing the current system, which is expensive and does not meet present production level needs.

THE INDUSTRY, ITS CHARACTERISTICS AND EFFLUENTS

The RIPASA S/A Celulose e Papel Company is located at Limeira, next to the Piracicaba River, in the State of São Paulo, Brazil. RIPASA produces 657 tons/day of pulp, with 95% bleached, and 220 tons/day of paper. Most of the paper produced is of the printing type. The wood used comes from trees of the Eucalyptus genus, grown in several plantations of the RIPASA Group. Pulp is obtained using the kraft process, as shown in Fig. 1, and the bleaching sequence adopted is C Eo H H (chlorination, oxidizing extraction, hypochlorination I, hypochlorination II).

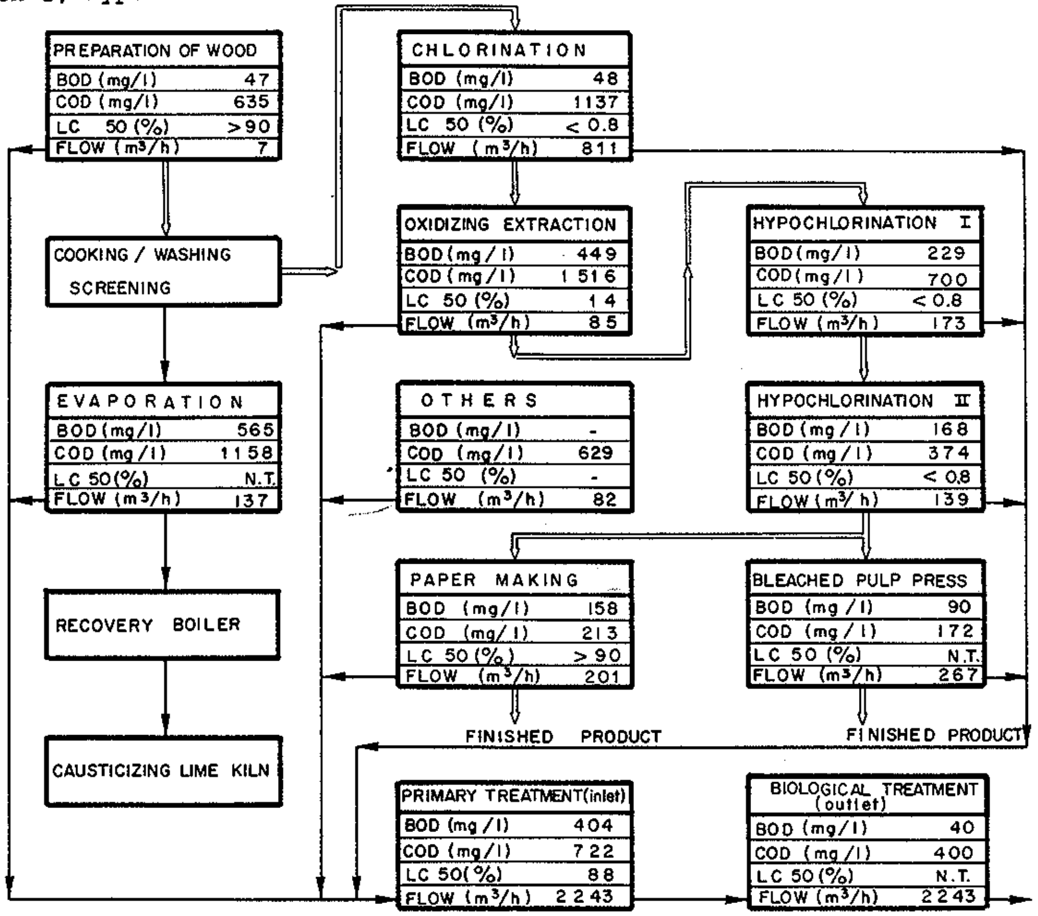


Fig. 1. Simplified flowchart of the industrial process, showing the origins and characteristics of the discharges (N.T. = non toxic)

The effluents generated by the production process derive from the wood preparation, evaporation, and bleaching stages, the bleached pulp press, and the paper-making stage. The qualitative and quantitive attributes of the effluents can be seen in Fig. 1. These effluents are divided into two lines, depending on whether they are acid or alkaline.

After all the plant effluents are collected they are led to the treatment system, currently consisting of primary treatment followed by biological treatment in an aerated pond. During primary treatment, suspended solids are removed by two parallel rectangular settling tanks, provided with mixing and flocculation chambers (where flocculating agents can be dispensed) to remove the lignin compounds which cause colour in these effluents. Biological treatment consists of an aerated pond with a detention time of approximately 2.7 days. The effluent is sprinkled at the entrance to the pond to lower the temperature from 49°C to 40°C. To avoid short-circuiting in the pond there is plastic canvas to guide the hydraulic flow which defines four zones, the last being used as a settling zone. Oxygen is introduced by 50 aerators of 25 HP. Approximately 20 tons of BOD enter the pond daily and, in order to comply with the legal requirements for final effluents, there is a further addition of around 800 kg/hour of pure oxygen.

TREATABILITY STUDIES

Treatability Assays

Introduction. The main function of a biological treatment process is to remove the dissolved organic matter in the wastewater through cell metabolism and synthesis of new cells. Biological processes vary according to the manner in which organic matter makes contact with the microfauna and whether or not molecular oxygen is present. Biological processes used in the treatment of pulp and paper industry effluents are normally aerobic biological processes and the most frequently used of these are activated sludge and settling ponds with mechanical aeration.

Degradation kinetics and design parameters. For the optimization and designing of a biological system, it is necessary to know the characteristics of the effluent, the biological degradation kinetics, and the factors which influence the efficacy of the system.

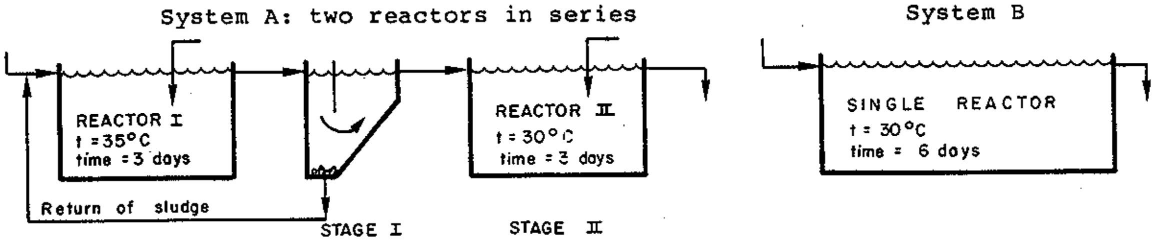
Eckenfelder and Ford (1970) proposed a mathematical model of the biological process and it is recommended that the parameters for use in the model be determined in laboratory or pilot units. The parameters required are the rate of biological degradation (k), oxygen consumption (a', b'), and sludge production (a, b). The biological degradation rate (k) is dependent on the effluent type and temperature and it can be determined by the following equation:

$$\frac{So - Se}{Xv \,.\, t} = k \,.\, Se$$

where: So = initial COD or BOD (mg/l); Se = final COD or BOD (mg/l); Xv = concentration of biological sludge in reactor (mg/l); t = detention time (days); k = biological degradation rate (1/day.mg).

The consumption of oxygen required for the process is obtained by a material balance using the parameters a' and b', where: a' = oxygen mass used for the production of cellular energy/total mass of substrate removed; and b' = oxygen mass required for endogenous respiration/biological sludge mass in the system (day). Accordingly, the production of biological sludge by the system is associated with the parameters a and b, where: a = sludge mass produced/total mass of substrate removed; and b = oxidized sludge mass/total mass of sludge existing in the system (day).

Pilot-scale assays. To obtain the design parameters, and also to assess the characteristics of the effluent after treatment, two pilot-scale systems were operated, fed with the effluent from the factory after primary settling. The first system (A) consisted of two biological reactors of 1000 litres, in series, with compressed air blown in through diffusers, interconnected by a secondary settling tank, the purpose of which was to return the settled sludge to the first reactor, keeping the sludge concentration around 300 mg/l. The detention time in each reactor was 3 days. The second system (B) consisted of a single reactor with compressed air blown in, with a detention time of 6 days. Schematics of these systems are shown in Fig. 2.


System A: two reactors in series

System B

Fig. 2. Schematics of the pilot systems

After acclimatization of the biological sludge, the systems were operated continuously, and daily follow-up analyses were undertaken, by means of composite samples taken from several parts of the system (COD, BOD, suspended solids, etc.).

As regards temperature, System A was operated with a controlled temperature: 35°C for the first reactor and 30°C for the second. System B was operated at 30°C. Nutrients were added to the effluent entering the systems, to maintain a BOD:N:P ratio of 100:5:1, and the pH of the reactors was kept at around 8. The pilot scale assays, all the studies on treatability, and collection and transport of the samples were performed by RIPASA's team. Samples for the assessment of toxicity were forwarded to CETESB for testing.

Results obtained. For the purposes of presentation and interpretation, analytical data were considered starting from the acclimatization period, when Systems A and B reached steady state. At steady state, assays were made of total and soluble COD and BOD at the outlet of the reactors (effluents) and of total COD and BOD at the inlet (influent). The mean values of these results, for each reactor, are shown in Table 1.

TABLE 1 Means Obtained for Systems A and B

	Influent		Effluent			
	Total COD, mg/l	Total BOD, mg/l	Total COD, mg/l	Total BOD, mg/l	Filtered COD, mg/l	Filtered BOD, mg/l
System A: reactor I	723	311	432	45	311	25
decanter	432	45	350	27	-	-
reactor II	350	27	310	15	276	11
System B: single reactor	723	311	406	37	284	13

For the purposes of calculating the biological degradation rate (k), the data were grouped in ranges of influent COD, followed by a calculation of mean values for the influent total and effluent filtered COD for each reactor, as well as values of volatile suspended solids (Xv), which are shown in Tables 2, 3 and 4. These tables also show values for (So - Se)/Xv.t.

TABLE 2 Means for Reactor I of System A at 35°C

Influent COD range, mg/l	Influent COD (So), mg/l	Effluent COD (Se), mg/l	Xv, mg/l	(So - Se)/Xv.t, day^{-1}
300 - 400	385	258	203	0.209
400 - 500	444	283	111	0.483
500 - 600	578	296	155	0.606
600 - 700	639	284	249	0.475
700 - 800	770	303	226	0.689
800 - 900	861	330	269	0.705

TABLE 3 Means for Reactor II of System A at 30°C

Influent COD range, mg/l	Influent COD (So), mg/l	Effluent COD (Se), mg/l	Xv, mg/l	(So - Se)/Xv.t, day^{-1}
250 - 300	291	257	39	0.291
300 - 350	329	271	60	0.322
350 - 400	372	275	57	0.567
400 - 450	426	295	72	0.597
450 - 500	474	334	58	0.805

TABLE 4 Means for Single Reactor of System B at 30°C

Influent COD range, mg/l	Influent COD (So), mg/l	Effluent COD (Se), mg/l	Xv, mg/l	(So - Se)/Xv.t, day^{-1}
400 - 500	444	261	233	0.262
500 - 600	569	299	228	0.395
600 - 700	639	299	267	0.424
700 - 800	774	305	254	0.615
800 - 900	855	331	254	0.688

Figs 3, 4 and 5 show the linear regression of plotted points of (So - Se)/Xv.t values (ordinates) versus Se (abscissae). The angular coefficient represents the biological degradation rate and r^2 the determination coefficient. The degradation rates found were as follows: System A - reactor I, K_{35} = 0.0072 $l.day^{-1}.mg^{-1}$, reactor II, K_{30} = 0.0053 $l.day^{-1}.mg^{-1}$; System B - single reactor, K_{30} = 0.0064 $l.day^{-1}.mg^{-1}$.

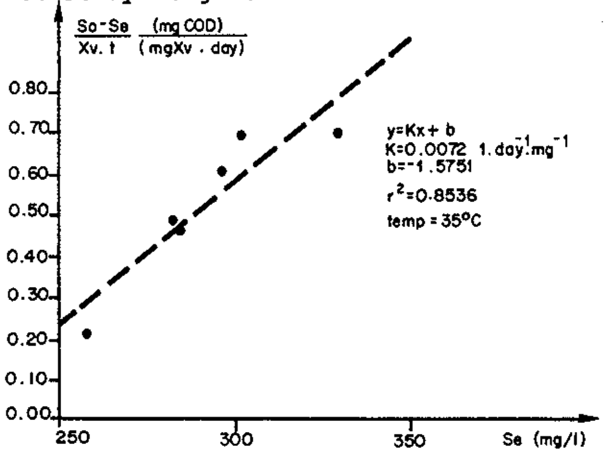


Fig. 3. Graphic determination of biological degradation rate (K_{35}) for reactor I of System A

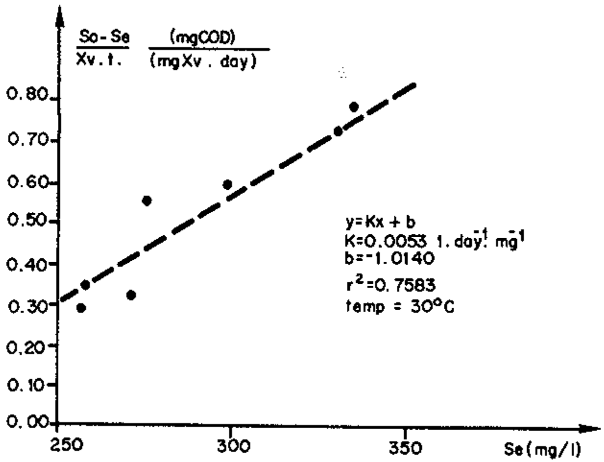


Fig. 4. Graphic determination of biological degradation rate (K_{30}) for reactor II of System A

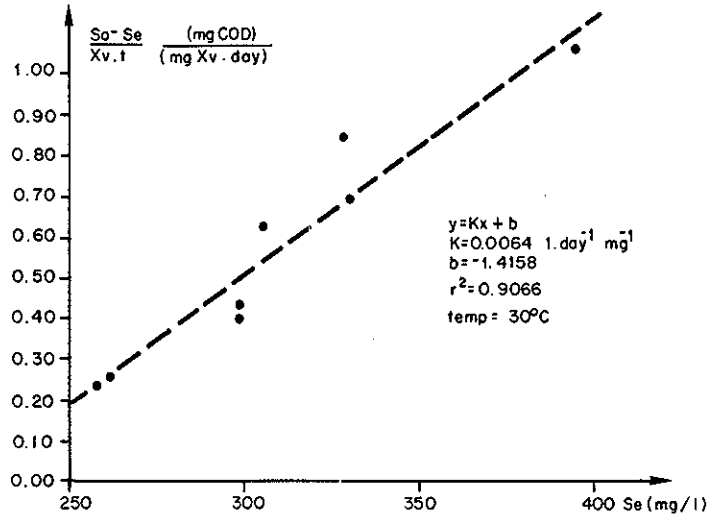


Fig. 5. Graphic determination of biological degradation rate (K_{30}) for single reactor of System B

EVALUATION OF TOXICITY

The toxicity of pulp and paper mill effluents has been widely investigated for the last twenty years. The acute toxicity level of effluents from this type of industry may vary from non toxic to highly toxic, depending mainly on the wood, the type of process, and the equipment employed, as well as on the treatment system adopted for each mill (Howard and Walden, 1965; Walden, 1976; Walden and Howard, 1977; Hattula et al., 1981; McLeay et al., 1986).

Sublethal effects may be detected in aquatic organisms as a consequence of extended exposure to these effluents (McLeay et al., 1986).

The final effluents from this industry are highly complex, and some of the substances they contain have already been identified and quantified. It is known that the main constituents responsible for the toxicity of these effluents are: resins, fatty acids, chlorinated phenolic compounds, and an extensive group of neutral compounds (Rogers, 1973; Rogers et al, 1975, 1979; Covillard, 1981). Furthermore, other variables may represent a hazard to aquatic organisms, such as pH, dissolved oxygen, colour, suspended solids (Hicks and DeWitt, 1971; Howard et al., 1979; McLeay et al., 1979; Graves et al., 1981). Toxicity tests have been used to evaluate the toxicity of in-plant effluents and their contribution to the final effluent, as well as the efficiency of the treatment system. These tests have been used together with other parameters to characterize industrial effluents and have proved useful for the control of these effluents in some countries, through various approaches (Anon., 1975; Pessah and Cornwall, 1980; Karbe, 1984; USEPA, 1984, 1985). In Brazil, the literature on toxicity evaluation and the impact of pulp and paper effluents on tropical ecosystems is very scarce (Rocha, 1985). Previous investigations undertaken at mills located in the State of São Paulo, Brazil (CETESB, 1977a, 1979, 1986a) indicate that treated effluents from kraft pulp and paper mills using Eucalyptus as the fibrous raw material may or may not cause an acute toxic effect on organisms and that the intensity of this toxic effect is not uniform.

Toxicity Tests

The toxicity of the effluents from in-plant processes and the final effluent before and after primary treatment was evaluated using 24 h composite samples with the microcrustacean Daphnia similis (ISO, 1982a, modified; CETESB, 1986c). The final effluent acute toxicity after biological treatment was evaluated with D. similis using the same method and also using the indigenous species of fish Cheirodon notomelas (ISO, 1982b, modified; CETESB, 1986c), on 24 h composite samples. The presence of chronic toxicity was investigated in these final effluents and in river water samples (collected upstream and downstream of the effluent discharge) using the microcrustacean Ceriodaphnia dubia (USEPA, 1985). The two microcrustacean genera have been easily raised and kept under laboratory conditions (Tunstall and Solinas, 1977; Schmaltz, 1979; Mount and Norberg, 1984; Lopez, 1986), they rank among the genera with the highest sensitivity to toxic substances, and they represent one of the richest food sources for other aquatic organisms, such as fish (Mount and Norberg, 1984).

The acute toxicity test results were expressed in terms of effluent concentration that causes 50% of the observed effect during the exposure time, i.e., immobility of D. similis, given as effective concentration (EC50, 24 hours, in %), and mortality of C. notomelas, given as lethal concentration (LC50, 48 hours, in %). When tests with D. similis showed a low percentage of the observed effects, i.e., 10% to 20% immobility of test organisms at the highest concentration, this effect was considered as 'signs of toxicity'. Chronic toxicity test results with C. dubia were expressed as the highest concentration of the effluent that causes no effect on reproduction and survival of test organisms, during 7 days of exposure (NOEC, in %).

Reconstituted soft water (APHA, 1985) was used as the dilution water for testing the effluents from the process and primary treatment. For testing the final effluents, after biological treatment, receiving water samples were collected upstream of the industrial discharge (Piracicaba River, hardness 20 mg/l in $CaCO_3$, pH 6.8).

To evaluate the contribution of each effluent generated by the industrial process towards the toxicity of the final effluent, values of LC50 obtained were transformed into toxic units (TU), i.e., 100/LC50. The toxic load of each effluent was obtained by the multiplication of TU data and average flow. Organic loads were also calculated, expressed as kg/day BOD and COD.

Impact estimates. To assess the impact of the final effluent, the concentration of effluent in the receiving water under minimum flow conditions was estimated, always assuming complete mixing of the effluent with the receiving water. These estimates were achieved using the expression (USEPA, 1985):

$$\text{IWC} = \frac{\text{Effluent flow}}{\text{Receiving water flow (7Q10)} + \text{effluent flow}} \times 100$$

where: IWC = instream water concentration, and 7Q10 = receiving water minimum flow. Calculated concentrations were compared with NOEC values, considering that the IWC should be equal or less than NOEC to prevent chronic effects on organisms in the receiving water.

Toxicity Test Results

The acute toxicity of the in-plant effluents to D. similis and the data on pH, average flow, toxic loads, and BOD and COD loads of each effluent tested are presented in Table 5. In Table 6, the acute and chronic toxicity test results from the biological treatment effluents are shown. Water samples from the Piracicaba River, collected upstream and downstream of the final effluent discharge have not indicated chronic effects in C. dubia. Table 7 shows the data for the estimates of the impact of the effluents on Piracicaba River.

DISCUSSION OF RESULTS

The effluents from RIPASA pulp and paper mill have undergone major qualitative and quantitative changes over the years. These changes were due to the constant modification of the production process, in order to use new and better quality technologies, and to increased production levels. An analysis of previous studies indicated a considerable reduction of specific organic loads had taken place. The 45 kg of BOD per ton of cellulose produced in 1977

TABLE 5 Acute Toxicity to Daphnia similis, Loads, and Flows of Various Process Effluents

Process effluent	EC50, %	TU	pH	Flow, m^3/d	Toxic load, $TU.m^3/d$	BOD load, kg/d	COD load, kg/d
Wood preparation	>90.0	<1.1	6.4	168	185	8	107
Evaporation	NT	0	7.3	3,288	0	1,867	3,807
Chlorination	<0.8	>125	2.2	19,464	2,433,000	9,518	22,131
Oxidizing extraction	14.0	7.1	11.2	2,040	14,484	916	2,093
Hypochlorination I	<0.8	>125	9.6	4,152	519,000	951	2,906
Hypochlorination II	<0.8	>125	9.4	3,336	417,000	560	1,248
Paper machine	>90.0	<1.1	6.0	4,824	5,306	762	1,028
Bleached pulp press	NT	0	7.0	6,408	0	576	1,103
Treatment influent	88.0	1.14	7.1	53,832	61,368	21,748	38,867

NT = non toxic

TABLE 6 Acute* and Chronic** Toxicity of Effluents from Treatment Systems Studied

	24 h EC50, %						48 h LC50, %		NOEC, %			
	1986		1987				1987		1987			
Sampling points	8/12	11/12	20/1	28/1	5/3	2/4	20/1	28/1	20/1	28/1	5/3	2/4
Primary treatment inlet	TS	88	TS	-	NT	-	-	-	-	-	-	-
Primary treatment outlet	>37	TS	TS	-	TS	-	-	-	-	-	-	-
Aerated pond outlet (current system)	NT	TS	-	NT	TS	NT	-	NT	-	NT	<5	50
Pilot system A reactor I outlet	TS	-	NT	-	-	-	NT	-	50	-	-	-
Pilot system A reactor II outlet	NT	-	NT	-	-	-	NT	-	NT	-	-	-
Pilot system B outlet	NT	-	NT	-	-	-	NT	-	10	-	-	-

* with D. similis (24 h EC50) and C. notomelas (48 h LC50); **with C. dubia (NOEC);
NT = non toxic; TS = signs of toxicity

TABLE 7 Effluent Impact Estimates for Piracicaba River

Effluents	Average flow, m^3/s	7Q10, m^3/s	IWC, %	NOEC, %	Potential for instream chronic toxicity*
Aerated pond (current)	0.55	21.6	2.5	5	No
Pilot system A	0.55**	21.6	2.5	NT***	No
Pilot system B	0.55**	21.6	2.5	10	No

7Q10 = receiving water minimum flow; IWC = instream waste concentration;
*When IWC $\succcurlyeq$ NOEC there is no potential for chronic effects on receiving water organisms;
**Estimated flow, if system is implemented in the future
***No evidence of chronic toxicity;

decreased to less than 30 kg of BOD per ton of cellulose produced in 1986. Table 5 shows the contribution of each industrial process stage in terms of organic load, expressed as COD and BOD. This table shows that bleaching is responsible for around 55% of the organic load of the final effluent, expressed as BOD. It further shows that effluents had various toxicity levels, with the highest toxicity levels being found at the chlorination and hypochlorination I and II stages, which confirms literature data (Howard and Walden, 1965; Betts and Wilson, 1966). McLeay et al. (1986), reviewing the toxicity to aquatic organisms of pulp and paper mill effluents, pointed out that replacement of the chlorination stage by chlorine dioxide in the bleaching process may increase the acute toxicity of effluents of industries using the bleaching kraft process.

There was also an attempt to verify, using data from Table 5, the existence of a correlation between effluent toxicity to D. similis and the physico-chemical analyses. These correlations were based on pH and toxic units data for the various processes and also on toxic loads, BOD, and COD data. The results indicated no significant correlation ($P = 0.05$) between the variables analysed. However, it should be stressed that the pH may modify the toxicity of substances present in effluents (Alabaster and Lloyd, 1980). The absence of correlation between the toxicity and chemical variables tested was also evidenced by the results of loads in the treatment system influent, where it could be seen that, after interaction of different process effluents, there was a tendency towards addition for BOD and COD, but this was not observed for toxicity, which is probably due to antagonism between the substances.

The identification of toxicity for each stage of cellulose pulp production may help in the selection of protective measures when the effluent treatment systems prove inefficient in removing toxicity. Such identification may reduce the costs of the search for a process to solve this problem, since effluent toxicity is seldom correlated with the physico-chemical variables used in the design and operation of industrial wastewater treatment systems.

RIPASA's current system operates under non-optimized conditions and to achieve the required reduction in the level of organic compounds it is necessary to supplement the aerated pond with pure oxygen. The residual organic load of the system amounts to around 2,300 kg BOD per day, with the overall efficiency reaching 90%, of which 15% is derived from primary treatment, through the removal of suspended solids. Approximate average values for the treatment system final effluent are: 40 mg/l of BOD and 400 mg/l of COD, and a pH around 7.5-8.0. Regarding the data on toxicity, raw and final effluents showed both 'signs of' and 'absence of' acute toxicity. Data from the literature show that aerated pond systems, when well dimensioned and well operated, are efficient in reducing acute toxicity, especially regarding fish (Rogers et al., 1975; Zanella and Bergen, 1980; McLeay et al., 1986). The data for the present treatment system (primary treatment plus an aerated pond), show that the toxicity of the effluent to D. similis was reduced on two occasions (Table 6). Considering the occurrence of acute toxicity signs in some of the samples of final effluent tested and the observations made by McLeay et al. (1986) that acute toxicity tests could be inadequate for monitoring residual or sublethal toxicity of industrial effluents or receiving water samples, some tests were performed with C. dubia. Table 6 shows that the present treatment system (aerated pond) indicated chronic toxicity in two of the three samples tested, even though it had only indicated 'signs of' or 'absence of' acute toxicity to fish and Daphnia. These variations in the results could be due to changes in the process and/or the type of wood used, and also failure of this treatment system in removing chronic toxicity, which deserves further investigation.

The current treatment system is to be replaced because of its failure to cope with current production levels, its high operational costs and its sensitivity to variations in organic loads. For optimization and design of the new system, a method of aerated pond dimensioning based on experimental parameters was used (Meiches et al., 1979). Pilot-scale studies indicated that when the effluents from the primary treatment are submitted to an aerobic treatment process, 6 days are enough to remove 88% and 95% of the BOD in the single-stage and two-stage systems, respectively, while removals of COD were 44% and 57%, respectively (data from Table 1). In designing of the treatment system it became clear that physico-chemical analyses, both of effluents generated during the production process and of the final effluent, are not sufficient for selection of alternative solutions. It is not possible to predict effluent toxicity, or even the removal of toxicity, by means of physico-chemical data. For this reason, toxicity played a major role in this study.

Concerning the pilot systems, treatment by System A removed acute and chronic toxicity, while System B only removed acute toxicity. Therefore, comparing the treatment systems studied, the two-stage system seems more capable of removing the toxicity of industrial wastewater. Jank et al. (1975) undertook some studies to evaluate the efficiency of activated sludge in the removal of toxicity from a pulp and paper mill effluent, and their conclusion was that the two-stage activated sludge system was more efficient in the reduction of toxicity compared with the single-stage system. As regards reduction of the organic load of the effluent and the treatability potential, a biological degradation rate (K) was determined, which is dependent on the type of substrate available in the industrial wastewater. The values found in this study, expressed in COD, are close to those obtained by previous studies reported by RIPASA and CETESB (CETESB, 1977b). Concerning parameters of oxygen consumption and sludge production, data from previous studies were adopted (CETESB, 1977b): a' = 0.71 and b' = 0.10 day^{-1}; a = 0.63 and b = 0.07 day^{-1}. These values are compatible with the values for pulp and paper mills using the kraft process with bleaching (Ramalho, 1977). Even though degradation rates (k) found in this study may differ when compared at the same temperature, it was demonstrated that as the substrate is exhausted, degradation of the remaining organic matter becomes more difficult, therefore leading to decreasing K values, as more biological reactors are connected. It was also shown that, although treated effluent filtered COD values were relatively high (around 55% of the influent COD values), the effluent BOD values were low (between 11 and 15 mg/l), which also indicates the difficult biological degradation of the organic substances which this type of wastewater contains. It is probable that some complex lignin compounds, responsible for the colour of the wastewater from this type of industry, may be extremely resistant to biological degradation. Pulp and paper mill effluents, even when submitted to colour removal processes, achieved removal rates of 72% BOD and 51% COD, after biological treatment at pilot scale (CETESB, 1977b; Grieco et al., 1979). These values, when compared to those obtained from this study, suggest that the levels of COD removal seem to be reaching the limits for conventional biological processes.

Besides the research regarding effluent treatability and toxicity there was special concern regarding the environmental impact of the wastewater on the receiving water. The impact evaluation was based on the fundamental principle that a certain toxic effect is a function of the toxicity of the effluent and of its estimated concentration in the receiving water. Therefore, by determining these variables, it becomes possible to evaluate the environmental hazards and to take the necessary measures to prevent toxic effects (USEPA, 1985). At present, this approach seems to be the most promising to be adopted by the State of São Paulo (CETESB, 1986a) since it does not set general discharge standards but leads to a more precise estimate of the potential toxic effects which aquatic organisms in different receiving waters will be subjected to.

In this way, the prediction of the impact of the effluents studied on the receiving water (Piracicaba River) was based on chronic toxicity data using C. dubia. In the case of RIPASA's current treatment system, the results chosen were those which showed the highest chronic toxicity (Table 7). As regards the diluting capacity of the receiving water, minimum flow conditions were considered (7Q10). The results obtained (Table 7) show that the industry's final effluents, after the treatment processes under study, will probably cause no chronic toxic effects in the organisms of the receiving water. Tests with C. dubia and samples from the receiving water, upstream and downstream of the discharge outlet, showed no chronic toxicity to this organism. Further supplementary studies are anticipated, with a continuing monitoring programme with the purpose of verifying the variation of toxicity of the treatment system effluent, as a function of variation in the quality of the wood used and changes in the production process.

CONCLUSIONS

- Samples from production process effluents showed different levels of acute toxicity, but the effluent as a whole showed low toxicity levels for the organisms tested.

- Final effluent samples collected from RIPASA's current treatment system do not cause a significant acute toxic effect in Daphnia similis or Cheirodon notomelas, but they do cause chronic toxicity in Ceriodaphnia dubia, which shows the importance of using these tests when acute toxicity is not observed. Concerning organic matter, BOD values were 40 mg/l and COD was around 400 mg/l, a removal of 90% of the BOD and 53% of the COD.

- The two-stage pilot system seems to be the best in terms of removal of chronic and acute toxicity, according to the samples studied. Removals of BOD and COD were 95% and 57%, respectively.

- Final effluents, both from the pilot system and from the current system, will probably cause no impact on the receiving water organisms, in terms of chronic toxicity.

- Biological degradation rates, based on COD, showed the difficulty of assimilation of the wastewater organic matter. The soluble organic matter had a COD/BOD ratio of 20, which suggests we are approaching the limiting conditions as regards the removal of organic material, since BOD mean values were around 11 to 13 mg/l when the wastewater was treated for 6 days by an aerobic biological process (aerated pond).

ACKNOWLEDGEMENTS

The authors particularly wish to thank Elenita Gherardi Goldstein for her review and valuable comments. We also thank Pedro Antonio Zagatto and Marisa Cury for their help with this paper. We acknowledge RIPASA's operational team who kindly provided data and information on the industrial process.

REFERENCES

Alabaster, J.S. and Lloyd, R. (Eds) (1980). Water Quality Criteria for Freshwater Fish. Butterworths, London.
Anon. (1975). Pollution Eau. Décrets et arrêtés du 28 octobre. No. 75-249. France.
APHA (1985). Standard Methods for the Examination of Water and Wastewater. 16th ed. APHA/AWWA/WPCF, New York.
Betts, J.L. and Wilson, G.G. (1966). New methods for reducing the toxicity of kraft mill bleachery wastes to young salmon. J. Fish. Res. Board Can., 23 (6), 813-824.
CETESB (1977a). Programa bioensaios - Relatório parcial no. 3. Companhia de Tecnologia de Saneamento Ambiental, São Paulo, SP.
CETESB (1977b). Sistema de tratamento dos resíduos líqüidos industriais da RIPASA S/A Celulose e Papel. Vol. II - Tratamento biológico. Companhia de Tecnologia de Saneamento Ambiental, São Paulo, SP.
CETESB (1979). Programa bioensaios - Relatório final anual. Companhia de Tecnologia de Saneamento Ambiental, São Paulo, SP.
CETESB (1986a). Avaliação da toxicidade de efluentes de indústrias de papel e celulose. Companhia de Tecnologia de Saneamento Ambiental, São Paulo, SP.
CETESB (1986b). Avaliação da toxicidade das águas, sedimentos dos rios e efluentes industriais de região de Cubatão. Companhia de Tecnologia de Saneamento Ambiental, São Paulo, SP.
CETESB (1986c). Desenvolvimento de métodos para o estabelecimento de critérios ecotoxicológicos. Relatorio final. 1983. Companhia de Tecnologia de Saneamento Ambiental, São Paulo, SP.
Covillard, D. (1981). Evaluation des impacts environnementaux dus aux rejets d'une usine de pate kraft sur le Salmo salar ouaniche à l'aide d'une nouvelle méthode: le graphe de cohérence. Environ. Poll. (ser. B), 2, 145-161.
Eckenfelder, W.W. and Ford, D.C. (1970). Water Pollution and Control: Experimental Procedures for Process Design. The Pembertton Press, Texas.
Graves, W.C., Burton, D.T., Richardson, L.B. and Margrey, S.L. (1981). The interaction of treated bleached kraft mill effluent and dissolved oxygen concentration on the survival of the developmental stages of the sheepshead minnow (Cyprinodon variegatus). Water Res., 15, 1005-1011.
Grieco, V.M., Lorenti, V.P.A., Campos, A.F.C.M. and Gomes, A.J. (1979). Remoção de cor em efluentes de fabricas de celulose e papel que utilizam processo kraft. 12º Congresso Anual da Associação Brazileira de Celulose e Papel, São Paulo, SP.
Hattula, M.L., Wasenius, V.M., Reunanen, H. and Arstila, A.V. (1981). Acute toxicity of some chlorinated phenols, catechols and cresols to trout. Bull. Environ. Contam. Toxicol., 26, 295-298.
Hicks, D.B. and DeWitt, J.W. (1971). Effects of dissolved oxygen on kraft pulp

mill effluent toxicity. Water Res., 5, 693-701.

Howard, T.E. and Walden, C.C. (1965). Pollution and toxicity characteristics of kraft pulp mill effluents. TAPPI, 48 (3), 136-141.

Howard, T.E., Malick, J. and Walden, C.C. (1979). Effluent color and algal impact. Pulp Paper Can., 80 (9), 291-295.

ISO (1982a). Water Quality: Determination of the Inhibition of the Mobility of Daphnia magna. Straus (Cladocera, Crustacea). International Organization for Standardization, Paris, Ref. No. 6341 - 1982 (E).

ISO (1982b). Water Quality: Determination of the Acute Lethal Toxicity of Substances to a Freshwater fish (Brachydanio rerio (Hamilton-Buchanan). Teleostei, Cyprinidae) - Part 1: Static Method. International Organization for Standardization, Paris (Draft International Standard ISO/DIS 7346/1, ISO/TC147).

Jank, B.E., Bisset, D.W., Cairns, V.W. and Metikosh, S. (1975). Toxicity removal from kraft bleachery effluent with activated sludge. Pulp Paper Can., 76 (4), 51-56.

Karbe, L. (1984). Biological monitoring of water in the Federal Republic of Germany. Regulatory approaches and methods for effluent testing and assessment of receiving waters. Proceedings of the International Workshop on Biological Testing of Effluents, Duluth, Minnesotta, pp. 123-132.

Lopez, J.S. (1986). Daphnia pulex bio-assay for toxicity control of effluent from kraft pulp mill in Spain. 19º Congresso Anual de Celulose e Papel, Semana do Papel, da Associacão Brazileira de Celulose e Papel, São Paulo, SP.

McLeay, D.J., Walden, C.C. and Mumro, J.R. (1979). Effect of pH on toxicity of kraft pulp and paper mill effluent to salmonid fish in fresh and sea water. Water Res., 13, 249-254.

McLeay, D.J., McKague, A.B. and Walden, C.C. (1986). Aquatic Toxicity of Pulp and Paper Mill Effluent. A Review. D.J. McLeay & Assoc. Ltd, W. Vancouver, BC.

Meiches, L.A.M., Grieco, V.M. and Centurión, R.E.B. (1979). Sistemática de dimensionamento para lagoas aeradas. 10º Congresso de Engenharia Sanitária e Ambiental, Manaus, AM.

Mount, D.I. and Norberg, T.J. (1984). A seven-day life-cycle cladoceran toxicity test. Environ. Toxicol. Chem., 3, 425-434.

Pessah, E. and Cornwall, G.M. (1980). Use of toxicity tests in regulating the quality of industrial wastes in Canada. In: Aquatic Toxicology. ASTM STP 707, J.G. Eaton, P.R. Parrish and A.C. Hendricks (Eds), American Society for Testing and Materials, pp. 130-141.

Ramalho, R.S. (1977). Introduction to Wastewater Treatment Processes. Academic Press, New York.

Rocha, A.A. (1985). Poluição por resíduos liqüidos de fábrica de papel e celulose, tipo kraft. Eng. Sanit., 24 (1), 116-120.

Rogers, I.H. (1973). Isolation and chemical identification of toxic components of kraft mill wastes. Pulp Paper Mag. Can., 74 (9), 111-116.

Rogers, I.H., Davis, J.C., Kruzynski, G.M., Mahood, H.W., Servizi, J.A. and Gordon, R.W. (1975). Fish toxicants in kraft effluents. TAPPI, 58 (7), 136-140.

Rogers, I.H., Mahood, H., Servizi, J. and Gordon, R. (1979). Identifying extractives toxic to aquatic life. Pulp Paper Can., 80 (9), 94-98.

Schmaltz, J.F. (1979). Can Daphnia replace fish for bioassays? Pulp Paper Can., 80 (7), 72-76, 225-228.

Tunstall, E.W. and Solinas, M. (1977). Daphnia pulex pulls its weight in pulp mill toxicity tests. Pulp Paper Can., 78 (4), 84-89, 93-97.

USEPA (1984). Technical Support Document for Water Quality-based Toxics Control (draft), Office of Water Enforcement and Permits (EN-336), United States Environmental Protection Agency, Washington DC.

USEPA (1985). Methods for Measuring the Acute Toxicity of Effluents to Freshwater and Marine Organisms: Environmental Monitoring and Support Laboratory, 3rd ed., Cincinnatti (EPA/600/4-85/013).

Walden, C.C. (1976). The toxicity of pulp and paper mill effluents and corresponding measurements procedures. Water Res., 10, 639-664.

Walden, C.C. and Howard, T.E. (1977). Toxicity of pulp and paper mill effluents: a review of regulations and research. TAPPI, 60 (1), 122-125.

Zanella, E.F. and Berben, S.A. (1980). Evaluation of methodologies for the determination of acute toxicity in pulp and paper effluents. TAPPI, 63, 77-82.