

# Intensification of the leachate treatment process of nitrocellulose production

Lucrécio Fábio Santos<sup>1\*</sup>, Adriano Francisco Siqueira<sup>2</sup>, Daniel Clemente Vieira Rêgo da Silva<sup>3</sup>, Teresa Cristina Brazil Paiva<sup>4</sup>, Flávio Teixeira da Silva<sup>5</sup>

<sup>1,2,4,5</sup> Department of Chemistry, Engineering School of Lorena, University of São Paulo (EEL/USP)

<sup>3</sup> Department of Chemistry, Federal University of the South and Southeast of Para (UNIFESSPA)

\*Corresponding Author

**Abstract**— Purification of cellulose is one of the most important steps in the production of nitrocellulose for explosives. However, it generates highly polluting wastewater. In this study, nitrocellulose industry wastewater (leachate) was characterized and treated chemically and biologically. Untreated leachate had a pH of  $12.4 \pm 0.5$ , color of  $27,065 \pm 879$  units, chemical oxygen demand (COD) of  $7,615 \pm 252$  mg/L, biological oxygen demand (BOD) of  $4,413 \pm 194$  mg/L, total organic carbon (TOC) content of  $2,455 \pm 158$  mg/L, total solids of  $8,613 \pm 232$  mg/L, fixed solids of  $3,845 \pm 103$  mg/L, and volatile solids of  $4,768 \pm 129$  mg/L and was toxic to *Escherichia coli* and *Artemia salina*. Industrial-scale chemical treatment followed by pilot-scale biological treatment reduced COD by 97%, BOD by 99%, and TOC by 97% and eliminated toxicity.

**Keywords**— Delignification, Explosives, Nitration, Treatment, Wastewater.

## I. INTRODUCTION

The discharge of untreated or inadequately treated wastewater into water bodies can cause serious damage to aquatic ecosystems. Wastewater may contain high levels of phosphorus, nitrogen, antibiotics, herbicides, pesticides, heavy metals, and organic matter [1-4]. Such contaminants have been associated with acute and chronic toxicity, endocrine-disrupting effects, and antibiotic resistance [4].

Several biological, chemical, and physical wastewater treatments have been proposed [5-10], but their implementation in industries is not always feasible from operational and economic points of view. Prior to biological treatments, wastewater may need to be treated chemically to reduce the negative effects of recalcitrant contaminants on biological agents [10-13]. Chemical treatments remove or convert contaminants through chemical reactions. Typical chemical processes include coagulation, precipitation, and chemical oxidation [5]. Chemical precipitation is achieved by using reagents capable of reacting and forming stable precipitates with contaminants. The precipitate can then be removed. Organic matter is transformed into carbon dioxide, water, and inorganic ions via degradation reactions involving oxidizing species, particularly hydroxyl radicals [11-13].

In biological treatments, contaminant removal is achieved by the action of microorganisms. The process is based on the self-regeneration of water bodies, whereby organic material is transformed into inert substances [12]. Activated sludge processes are the most commonly used biological treatments. Aerobic microorganisms digest organic matter and form flocculated particles (active sludge) and a liquid practically free of suspended solids and organic material. The organic matter is broken down via biological oxidation, resulting in  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ , energy, and other products [12, 13]. Activated sludge treatment can be combined with other processes to improve the quality of the final effluent [10-13].

Textile, paper, and explosives wastewaters are opaque and have a high color because of the presence of lignin and its derivatives. In water bodies, these industrial wastewaters prevent light penetration and, consequently, photosynthesis. Furthermore, they contain high amounts of organic matter and toxic chemicals [14, 18, 32].

Nitrocellulose is the main raw material used to produce nitroglycerin, an explosive liquid present in smokeless gunpowder, propellants, and dynamites. Nitrocellulose production involves the following steps: mechanical separation, delignification, and bleaching of cotton fibers, nitration of cellulose, and stabilization of nitrocellulose [16]. The delignification process generates

leachate containing up to 10,000 mg/L of lignin, determined as soluble and insoluble Klason lignin. Lignin degradation products, such as hemicelluloses, extractives, and proteins, are also released during the delignification step [16, 19-26]. Resin and fatty acids from extractives and lignin degradation products are responsible for the high chemical oxygen demand (COD), biochemical oxygen demand (BOD), toxicity, and color in nitrocellulose industry wastewater [22].

This study aimed to characterize and intensify of the treatment of the leachate to reduce its color, organic load, and toxicity by integration of processes: chemical followed by biological treatment.

## II. MATERIALS AND METHODS

Nitrocellulose industry leachate was collected and stored according to the National Guide for Sample Collection and Preservation [27]. Treated and untreated leachate was characterized following the Standard Methods for the Examination of Water and Wastewater [28], with modifications. Toxicity tests using *Escherichia coli* and *Artemia salina* were carried out in triplicate according to the methods described by Garden et al. (1990) [29] and Hartl and Humpt (2000) [30], respectively, with modifications.

### 2.1. Acute toxicity assay

*E. coli* was cultured in medium containing  $K_2HPO_4$ ,  $KH_2PO_4$ , trisodium citrate,  $(NH_4)_2SO_4$ , and  $MgSO_4$  diluted in 800 mL of deionized water to the concentrations shown in Table 1.

Table 1: Composition of the culture medium used for *Escherichia coli*

Compound	Concentration (g/L)
$K_2HPO_4$	7.0
$KH_2PO_4$	3.0
Trisodium citrate	0.5
$(NH_4)_2SO_4$	1.0
$MgSO_4$	0.2
D-Glucose	4.0

Source: Authors, 2020.

The culture medium was placed in a microwave oven and boiled for 10 min. A 200 mL solution of 10% (w/v) glucose was prepared and boiled for 5 min. The two solutions were cooled to 90 °C and mixed, and the pH was adjusted to  $7.0 \pm 0.2$  using 4 mol/L NaOH.

A 100 mL stock solution containing 100 mmol/L  $Na_2CO_3$  (previously oven dried at 120 °C for 1 h) was prepared and diluted to obtain 0.25, 0.50, 1.0, 2.0, and 3.0 mmol/L solutions. Aliquots of 135  $\mu$ L were used to construct a calibration curve using a conductometry system [29]. The culture medium was inoculated with *E. coli*, and  $CO_2$  concentration was monitored until reaching 0.5 mmol/L. The initial pH of the samples was adjusted to  $7.0 \pm 0.2$  using 1 mol/L NaOH or 1 mol/L  $H_2SO_4$ . Leachate was added to culture flasks at concentrations of 2, 6, and 10%, and  $CO_2$  measurements were taken at 30 min intervals. The experiment lasted for 3 h.

### 2.2. Chronic toxicity assay

*A. salina* cysts (eggs) were incubated in 3.8% (w/v) NaCl in deionized water at 28–30 °C under a 60 W fluorescent lamp for 24 h. After hatching, larvae were separated and placed in 5 mL vials containing 1 mL of saline solution. Vials contained 10 larvae each and received the addition of 1.5 or 3.0 mL of leachate, corresponding to 30 and 60% (v/v), respectively. Vials were then filled to 5 mL with saline solution and incubated for 24 h at 28–30 °C. A control vial was prepared and subjected to the same conditions but without the addition of leachate. Dead and live larvae were counted in each vial, and results were expressed as the percentage of dead larvae [30].

### 2.3. Industrial-scale chemical treatment of leachate

Leachate is transported from the nitrocellulose production plant to the treatment plant via a 4-inch PVC pipe. The liquid is sieved (SS) and is discharged, by gravity, into the reservoir tank (RT). Then, it is pumped into RST 1 and RST 2, which are operated alternatively in batch. In RSTs, leachate is acidified to pH < 1.5 using the acid wastewater from the nitration step or, when not available, sulfuric acid. Solutions are mixed using air diffusers. After 2 h, the supernatant follows to the compartmentalized tank for coagulation (CT), pH adjustment (AT), flocculation (FT), and decantation (ST). Solids retained in the decanter are sent to a filter press (FP). The filtered liquid returns to the treatment system, and the sludge is directed to the final treatment step at the outlet of the decanter. The chemically treated leachate is then subjected to biological treatment using an activated sludge process in a sequencing batch reactor.

#### 2.3.1. Chemical treatment

Fig. 1 shows a scheme of the treatment system used for the chemical treatment of leachate. The system has a capacity for processing 40 m<sup>3</sup>/h. The project was designed on the basis of experimental bench-scale results. The reaction and settling tanks (RST 1 and RST 2) were

designed taking into account the decanting time. Flow, hydraulic retention time, and other process parameters were taken into account in the design of the coagulation,

alkalization, flocculation, and settling tanks, according to literature data [11-13].

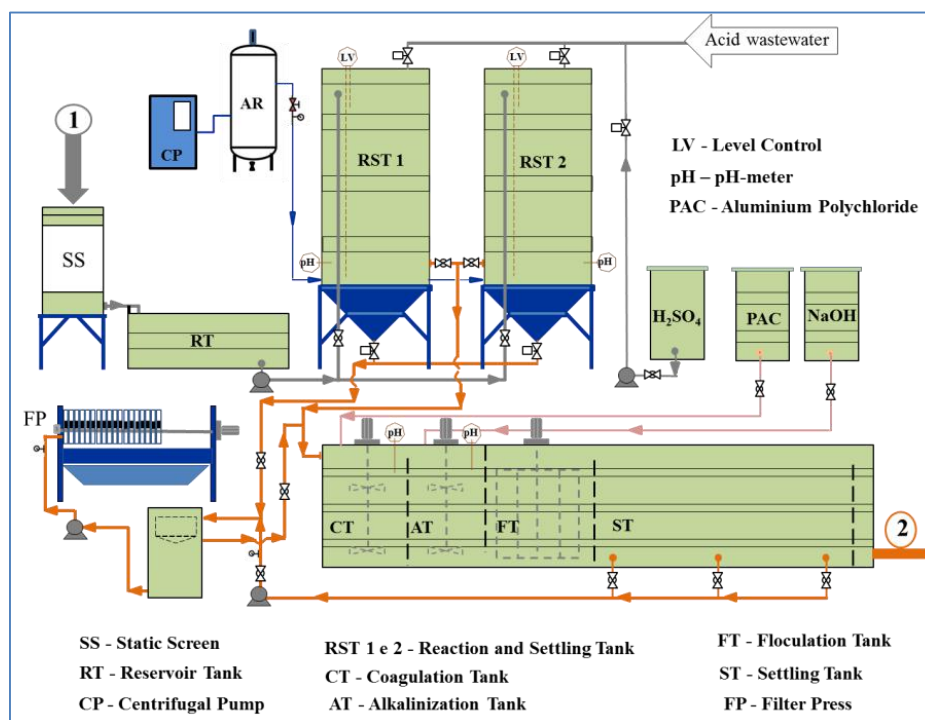


Fig.1: Industrial chemical system for treatment of nitrocellulose leachate

Source: Authors, 2020.

## 2.4. Pilot-scale biological treatment

Biological reactions were carried out in a 500 L stainless steel reactor (Fig. 2) equipped with three valves and operated in sequencing batch mode with 6 h cycles consisting of fill, react, settle, and draw periods. The time for sludge sedimentation ranged from 20 to 30 min [12]. Air was supplied to the system using an air compressor and diffusers.

The airflow was adjusted to provide a minimum oxygen concentration of 3 mg/L and ensure that the microbial biomass remained in suspension during the entire reaction period. Prior to the reaction, the pH of leachate was adjusted to  $7.0 \pm 0.3$  with 10% (w/v) NaOH solution. pH (B-374 pH-meter, Micronal, São Paulo, Brazil), dissolved oxygen (TO 401 analyzer, Digimed, São Paulo, Brazil), and temperature were monitored throughout the process [13].

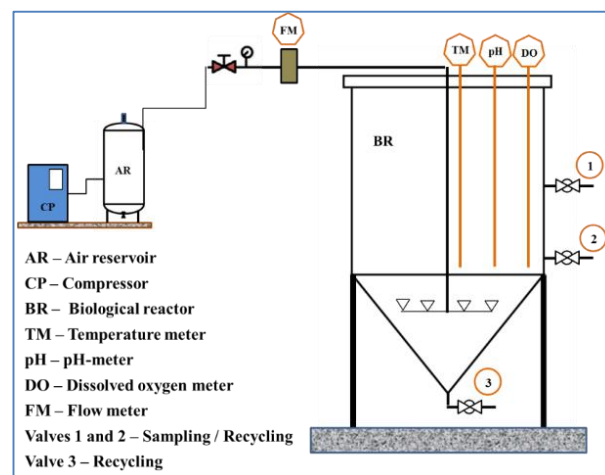


Fig.2: Schematic diagram of the biological reactor

Source: Authors, 2020.

## III. RESULTS AND DISCUSSION

Table 2 presents the physicochemical characteristics of leachate before and after industrial-scale chemical treatment and pilot-scale biological treatment.

Table 2: Physicochemical characteristics of untreated, chemically treated, and chemically and biologically treated leachate

Parameter	Untreated	Chemically treated	Chemically and biologically treated
pH	12.4 ± 0.5	7.1 ± 0.3*	7.1 ± 0.3*
Color (units)	27,065 ± 879	1,988 ± 84	2,113 ± 132
COD (mg/L)	7,615 ± 252	908 ± 38	198 ± 17
BOD <sub>5,20</sub> (mg/L)	4,413 ± 194	369 ± 14	43 ± 7
TOC (mg/L)	2,455 ± 158	153 ± 10	83 ± 7
TS (mg/L)	8,613 ± 232	3,472 ± 86	288 ± 13
FS (mg/L)	3,845 ± 103	1,540 ± 49	176 ± 16
VS (mg/L)	4,768 ± 129	1,932 ± 76	112 ± 9
N (mg/L)	25 ± 6	1.9 ± 0.2	4.7 ± 0.6
P (mg/L)	<5	<5	<5

Results are presented as mean ± standard deviation. \* The pH was adjusted to 7.0 ± 0.3 with 10% (w/v) NaOH solution before the reaction. COD, chemical oxygen demand; BOD<sub>5,20</sub>, biochemical oxygen demand (5 days at 20 °C); TOC, total organic carbon; TS, total solids; FS, fixed solids; VS, volatile solids; N, nitrogen; P, phosphorus.

Source: Authors, 2020.

Untreated leachate had a very high color intensity (27,065 ± 879 color units), COD (7,615 ± 252 mg/L), BOD<sub>5,20</sub> (4,413 ± 194 mg/L), and TOC content (2,455 ± 158 mg/L). The COD/BOD ratio was 1.73, indicating that leachate is susceptible to biological degradation [11]. Nevertheless, an industrial chemical process was used before biological treatment.

Chemical treatment decreased color intensity by 93%, COD by 88%, BOD<sub>5,20</sub> by 92%, and TOC by 94%. After biological treatment, COD was reduced by 97%, BOD<sub>5,20</sub> by 99%, and TOC by 97% compared with untreated leachate. No changes in color intensity were observed, suggesting that activated sludge is not effective in removing or degrading color compounds present in nitrocellulose leachate. Chemical processes, such as coagulation, are widely used as tertiary treatment for the removal of suspended solids, organic matter, and phosphorus [31, 32].

However, in this study, the chemical process was used to intensify the biological process for the treatment of leachate from nitrocellulose production. Fig. 3 and 4 show the effects of integrated treatment.

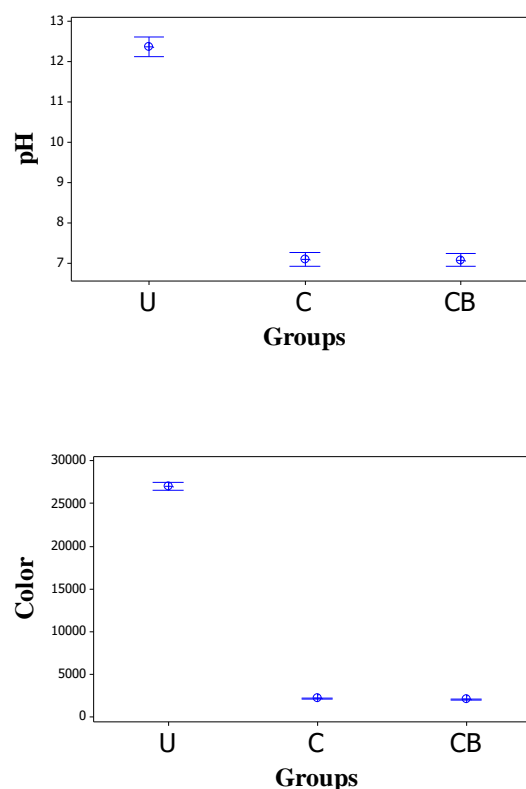


Fig.3: pH and color. The circle is the mean and the lines above and below are the 95% confidence intervals.

Source: Authors, 2020.

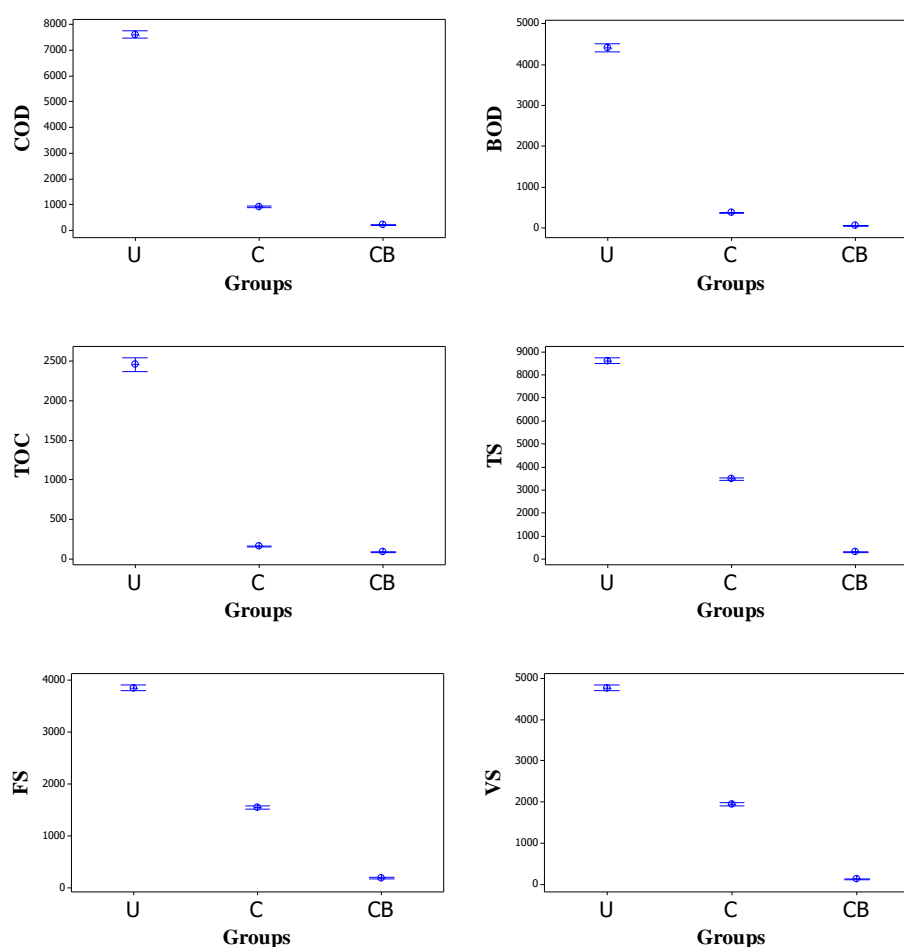


Fig.4: Chemical oxygen demand (COD), biochemical oxygen demand (BOD), total organic carbon (TOC) content, total solids (TS), fixed solids (FS), and volatile solids (VS) in untreated (U), chemically treated (C), and chemically and biologically treated (CB) leachate. The circle is the mean and the lines above and below are the 95% confidence intervals.

Source: Authors, 2020.

BOD<sub>5,20</sub> values of untreated leachate ( $4,413 \pm 194$  mg/L) were well above those commonly reported for domestic sewage (300 mg/L)[12, 13, 33, 34]. This parameter is widely used to indicate whether wastewater is suitable for discharge. Therefore, a model was developed to predict the BOD of biologically treated leachate (Eq. 1).

$$\text{BOD} = 4027.73 - 1.05 \times \text{COD}_u + 7.17 \times 10^{-5}(\text{COD}_u)^2 - 1.19 \times 10^{-5}\text{COD}_u\text{FS}_c \quad (1)$$

where COD<sub>u</sub> is the chemical oxygen demand of untreated leachate and FS<sub>c</sub> is the fixed solids content in chemically treated leachate. The analysis of variance for the proposed model is presented in Table 3.

Table 3: Analysis of variance for the model

Source	df	Seq SS	Adj SS	Adj MS	F	P
Regression	3	629.59	629.589	209.863	4.16747	0.0284069
COD <sub>u</sub>	1	31.53	245.346	245.346	4.87209	0.0458797
COD <sub>u</sub> × FS <sub>c</sub>	1	337.00	301.819	301.819	5.99354	0.0293136
COD <sub>u</sub> × COD <sub>u</sub>	1	261.06	261.059	261.059	5.18413	0.0403523
Error	13	654.65	654.646	50.357		
Total	16	1284.24				

Source: Authors, 2020.



All model parameters were significant at  $P < 0.05$ . A P-value of 0.27 was obtained for the Anderson–Darling statistic, ruling out the hypothesis of normality of data. This result indicates that the model can adequately predict BOD values after biological treatment. With an  $R^2 = 0.49$ , the model shows that the characteristics of untreated and chemically treated leachate influence the performance of biological treatment.

We calculated the 95% confidence intervals for experimental results and model predictions (Fig.5). The model indicates that the combined treatment can reduce BOD to less than 60 mg/L.

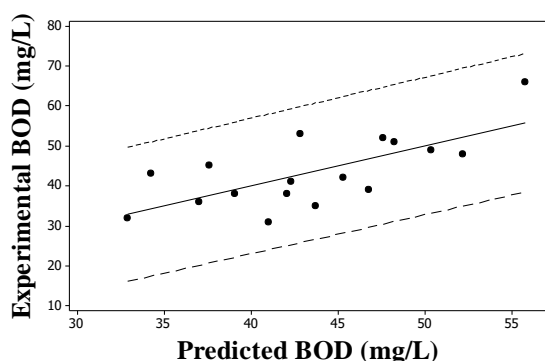


Fig.5: Experimental and predicted biochemical oxygen demand (BOD) of leachate after chemical and biological treatment. Black dots are experimental points, the solid line is the best fit, and the dashed lines are the 95% confidence intervals.

Source: Authors, 2020.

The acute toxicity of untreated leachate was assessed using *E. coli*. Black pulp at 2% immobilized 69% of microorganisms. At 6 and 10%, leachate completely immobilized *E. coli*. After chemical treatment, bacteria mobility was not affected by 2% leachate. At 6 and 10%, chemically treated leachate decreased bacterial mobility by 16 and 50%, respectively. Biologically treated leachate did not affect *E. coli* mobility.

Untreated leachate at concentrations of 30 and 60% showed chronic toxicity to *A. salina*, killing all microorganisms. Toxicity was not fully eliminated by chemical treatment. At 30 and 60%, chemically treated leachate killed 36 and 62% of micro crustaceans, respectively. Wastewater treatment should eliminate as many toxic compounds as possible, as contaminants are generally carcinogenic [35, 36]. The complexity of wastewater composition can further increase its recalcitrance to degradation [35]. Chemical treatment, despite reducing the organic load of leachate by more than 90%, was not sufficient to eliminate toxicity. Therefore, a

second treatment was necessary. After treatment with activated sludge, leachate was not toxic to *A. salina* at the tested concentrations.

The toxicity of leachate to the two microorganisms was probably due to the high concentration of organic matter and the presence of high molecular weight compounds (>kDa) derived from lignin. The recalcitrance to activated sludge treatment may be related to the limited ability of microorganisms to metabolize high molecular weight compounds [19, 20].

Nitrocellulose industry wastewater is highly toxic to the environment because it contains chlorophenols, chlorolignins, organic acids, acid resins, and dioxins [23, 32], as well as high levels of organic matter and metal ions [22]. There are few studies analyzing the toxicity of nitrocellulose to aquatic organisms [37-39], but many studies reported the detrimental effects of other explosives, such as 2,4,6-trinitrotoluene (TNT), 1,3,5-Trinitroperhydro-1,3,5-triazine (RDX), and 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX) [40-46].

#### IV. CONCLUSION

Leachate had high levels of lignin and organic matter, as evidenced by the high COD ( $7,615 \pm 252$  mg/L), color intensity ( $27,065 \pm 879$  units), and toxicity to *E. coli* and *A. salina*, which indicates that this wastewater can cause serious environmental contamination if released untreated.

Industrial chemical treatment reduced color intensity by 93%, COD by 88%, BOD by 92%, and TOC content by 94%. However, these reductions were not sufficient to meet regulatory requirements for wastewater discharge. Therefore, chemically treated leachate was subjected to a biological treatment with activated sludge, which reduced COD ( $198 \pm 17$  mg/L), BOD ( $43 \pm 7$  mg/L), and TOC content ( $83 \pm 7$  mg/L) to levels below regulatory limits. Chemical treatment did not eliminate toxicity but increased the susceptibility of leachate to biological treatment. Overall, the results show that integrated chemical and biological processes are promising for the remediation of leachate.

All wastewater generated by the pulp nitration step was reused for pH correction in the leachate treatment process. The reuse of the effluent from the nitration step made it possible to reduce the expenses with reagents for pH correction of this effluent before its release into the environment.

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