

REDUCING PRODUCTION OF EXCESS ACTIVATED SLUDGE IN BLEACHED KRAFT PULP MILL EFFLUENT TREATMENT

Teynha V. Stoppa, Ann H. Mounteer¹, Pedro H. G. Alves, Frederico H. C. Gomes

Environmental Engineering, Department of Civil Engineering, Federal University of Viçosa, Brazil

ABSTRACT

Treatment and disposal of waste sludge significantly impacts operating costs and environmental sustainability of the activated sludge process, one of the most widely used effluent treatment systems in Brazilian kraft pulp mills. Therefore, use of the chemical supplements folic acid and 3,3',4',5'- tetrachlorosalicylanilide (TCS) for reducing sludge production was investigated using laboratory bench-scale sequencing batch reactors. Folic acid (0.5 mg/L) reduced sludge yield by 24%, while TCS (1.0 mg/L) reduced yield by 19%, without negatively affecting COD removal efficiency, under varying organic loading rates. Sludge settleability was unaffected or improved at the optimum supplement doses. However, both supplements increased sludge specific oxygen uptake rates and hindered removal or increased effluent toxicity during biological treatment. Therefore, the decision to use either supplement in an existing activated sludge plant must consider available aeration capacity and effluent dilution in receiving waters.

Keywords: *eucalypt, folic acid, TCS, toxicity, treatment efficiency*

1. INTRODUCTION

The activated sludge process is one of the most widely used effluent treatment processes in kraft pulp mills because of its flexibility and reliability, especially when high quality effluents are required but little area is available (Metcalf & Eddy, 2003). However, this process has the drawback of generating the largest quantities of waste sludge among conventional biological treatment processes (Grady et al., 1999).

The Brazilian pulp and paper industry has undergone continued growth over the past several years and produced over 14 million tons of pulp in 2011 (BRACELPA, 2012). This growth, associated with widespread use of activated sludge systems has increased problems of waste sludge generation and disposal. In the activated sludge process, 5 to 15 kg of dry sludge are produced per ton of pulp (Elvira et al., 2006), meaning that a pulp mill that produces one million tons of pulp per year, can produce up to 15 000 tons of dry waste sludge per year.

The amount of sludge generated during biological effluent treatment, its treatment, reuse and, or correct disposal by economically viable and environmentally sustainable means are currently one of the most complex problems in the area of waste treatment at pulp mills. According to Saby et al. (2003), waste sludge treatment can represent from 30 to 60% of effluent treatment plant operating costs. Therefore, low cost alternatives for treatment and disposal of waste sludge and technologies to reduce waste sludge production are of interest. Technologies that have been proposed for reducing sludge production include thermal treatment (Yan et al., 2008; Laurent et al., 2011), chlorination (Takdastan et al., 2009; Wang et al, 2011), ozone treatment (Debellefontaine et al., 2007; Dytczak et al., 2007), ultrasound treatment (Yongde et al., 2009; He et al., 2011), addition of folic acid (Akerboom et al., 1994; Dubé et al., 2002) and addition of metabolic uncouplers (Rho et al., 2007; Chong et al., 2011). Most of these treatments have only been evaluated with domestic or synthetic effluents.

When folic acid (vitamin B9) is added to a biological effluent treatment system, the microorganisms present no longer need to synthesize this essential vitamin, resulting in repression of some metabolic pathways and acceleration of others (MOHR, 1987). The exact mechanism of how folic acid reduces excess sludge production is still not entirely known and there is scarce information available in the scientific literature (Ponezi, 2005). Strunkheide (2004) suggests a relationship between increased metabolic activity and reduced sludge production because of more complete sludge digestion in the treatment plant. Since addition of folic acid accelerates metabolic processes, it leads to greater endogenous respiration without the need to increase sludge mean cell residence time.

The use of metabolic uncouplers for sludge reduction is based on the fact that cell yield is directly proportional to the quantity of energy (ATP) produced during catabolism (ELVIRA *et al.*, 2006). Active microbial cells generate energy in the form of ATP which is consumed in growth and maintenance reactions by oxidizing organic compounds in the process known as cellular respiration. The energy for ATP is synthesized in the microbial cell membrane protein ATPase from ADP and inorganic phosphate, using energy supplied by the oxidation-reduction (redox) reactions of the electron transport chain. Metabolic uncouplers inhibit ATP synthesis by impeding the energy produced through the respiratory chain redox reactions from being used in phosphorylation of ADP. This energy is lost in the form of heat. In the presence of uncouplers, substrate consumption is higher than required for growth and maintenance under normal conditions. The microbial cells tend to increase their catabolic metabolism in an attempt to satisfy their energy requirements. Since this does not occur, the result in the effluent treatment system is reduced sludge production without decreased efficiency of organic substrate removal (Liu and Tay, 2001).

Uncouplers that have been studied for reducing sludge production include various nitro and chlorophenols (Mayhew and Stephenson, 1998; Low *et al.*, 2000; Hiraishi and Kawagishi, 2002). More recently, the use of 3,3',4',5'- tetrachlorosalicylanilide (TCS) have been proposed (Ye and Li, 2005; Rho *et al.*, 2007). TCS is frequently used in formulation of cleaning products such as shampoos and soaps and its indication for use in effluent treatment is stems from its lower toxicity than the phenolic uncouplers previously studied.

The objective of this study was to perform a comparative laboratory evaluation of the use of folic acid and TCS for reducing sludge production during activated sludge treatment of kraft pulp mill effluent. Specific objectives included comparison of treatment efficiencies and effluent toxicities in the presence of the chemical supplements.

2. METHODS

2.1. Effluent and sludge

Effluent was collected after primary treatment at a bleached eucalypt kraft pulp mill. Sludge was collected from the sludge recycle line of the activated sludge treatment plant at the same mill. Effluent and sludge samples were transported to the Federal University of Viçosa Sanitary and Environmental Engineering Laboratory. The sludge was kept under constant aeration at room temperature and the effluent was stored at 4°C under a nitrogen atmosphere until use.

2.2. Biological effluent treatment

Five bench-scale sequencing batch reactors (SBR) with two liter working volumes were used to simulate activated sludge treatment in the laboratory. The SBRs were inoculated with 1000-1200 mg VSS.L⁻¹ return sludge and fed with primary effluent. Temperature was maintained at 30°C using submerged thermostats and dissolved oxygen at 4.0 mg.L⁻¹ by bubbling air through porous stone aerators placed at the bottom of the reactors. Hydraulic retention time (HRT) was 12 hours, with 11 hours aeration and one hour sedimentation, followed by withdrawal of treated effluent. Activated sludge mean cell residence time (MCRT) was kept at 10 days by daily wasting of 10% of the total suspended solids.

In preliminary studies with folic acid, the effluent added at the beginning of each cycle was supplemented with 0 (control), 0.5; 1.0; 2.0 or 4.0 mg.L⁻¹. In preliminary studies with TCS, the effluent was supplemented with 0 (control), 0.5; 1.0; 2.0 or 2.5 mg.L⁻¹ TCS. In a second step, three reactors were operated in parallel, one served as control; one was supplemented with folic acid and the third with TCS. Folic acid and TCS were added at the doses that resulted in the lowest sludge production in the preliminary studies. The reactors were operated under the same conditions as in the preliminary studies, but fed with varying organic loads, typical of bleached kraft pulp mill effluents.

2.3. Chemical analyses

Volatile suspended solids (VSS), chemical oxygen demand (COD) and sludge volumetric index (SVI) were analyzed according to the Standard Methods (APHA, 2012). Dissolved oxygen was measured using an oximeter equipped with membrane electrode (Digmec, model DM4, São Paulo).

2.4. Sludge production

Daily excess sludge production (P_X , g/d) was obtained from the relationship between mass of suspended solids in the SBR and sludge MCRT using Equation (1) (Metcalf & Eddy, 2003).

$$P_X = \frac{X.V}{MCRT} \quad (1)$$

where: P_X = daily excess sludge production, g.d⁻¹;
 X = sludge concentration in SBR, gVSS.m⁻³;
 V = SBR volume, m³;
 MCRT = sludge mean cell residence time, d.

Observed sludge yield (Y_{obs}) was calculated as the ratio of sludge production to COD removal, Equation (2).

$$Y_{obs} = \frac{P_X}{\Delta COD} \quad (2)$$

where: Y_{obs} = observed cell yield, gVSS produced.(gCOD removed)⁻¹;
 P_X = sludge produced, gVSS;
 ΔCOD = organic matter removed, gCOD.

Sludge specific oxygen uptake rate (SOUR, mgDOgVSS⁻¹h⁻¹) was quantified by the US Environmental Protection Agency method (USEPA, 2001).

Sludge production and SOUR in the different reactors were compared by analysis of variance (ANOVA) followed by comparison of means using the Tukey test at a 5% level of significance ($\alpha = 0.05$). Before performing statistical comparisons, data normality was checked using the Kolmogorov-Smirnov and Shapiro-Wilk tests. When necessary, data were normalized using the inverse square root transformation before performing ANOVA ($X' = 1/\sqrt{X}$).

2.5. Toxicity assays

Effluent toxicity was evaluated at the Federal University of Viçosa's Water Quality Control Ecotoxicology Laboratory using the *Pseudokirchneriella subcapitata* 72 hour algal growth inhibition (method 8112). Test organisms were originally acquired from the São Paulo State Environmental Sanitation Technology Company (CETESB) and cultures have been maintained for toxicity bioassays at the Ecotoxicology Laboratory for over four years. Organism sensitivity was monitored by periodically measuring toxicity to the reference substance copper sulfate. *P. subcapitata* results were expressed as the 72 h IC₂₅ (%), the effluent concentration that inhibited algal growth by 25%, estimated using a linear interpolation method available from the US EPA (2003). Toxicity units were calculated as 100/IC₂₅, so that effluent that caused greater growth inhibition presented a higher number of toxic units.

3. RESULTS AND DISCUSSION

3.1. Preliminary studies

Figure 1 presents the effect of folic acid and TCS addition on COD removal efficiency, observed sludge yield (Y_{obs}), specific oxygen uptake rate (SOUR) and sludge volume index (SVI) during aerobic biological treatment of kraft pulp mill effluent with an initial COD of approximately 1100 mg/L.

COD removal efficiencies were unaffected, except at the highest supplement doses evaluated. Upon addition of 4 mg/L folic acid COD removal fell from 77 to 71% ($p < 0.05$) while addition of 2,5 mg/L TCS reduced COD removal from 73 to 69% ($p < 0.05$). Chen et al. (2004) and Ye & Li (2005) reported that efficiency was not affected after addition of up to 3,7 mg/L TCS in treatment of domestic effluent.

Y_{obs} , which quantifies the true growth yield minus the endogenous decay of biomass in the reactor, was reduced ($p < 0.05$) by 24% at a dose of 0.5 mg.L⁻¹ folic acid and by 19% at TCS doses ≥ 1.0 mg.L⁻¹. Addition of ≥ 2.0 mg.L⁻¹ folic acid led to an increase in Y_{obs} , whereas the yield reduction remained constant with increasing TCS doses. Dubé et al. (2002) also found that 0.5 mg/L folic acid was able to reduce sludge yield during treatment of pulp mill effluent. Chen

et al. (2002) and Rho et al. (2007) observed reductions of 60 and 40% in Yobs values during treatment of synthetic domestic effluent with application of 0,4 and 0,8 mg.L⁻¹ TCS, respectively. Rho et al. (2007) also observed constant Yobs reduction with increasing TCS doses.

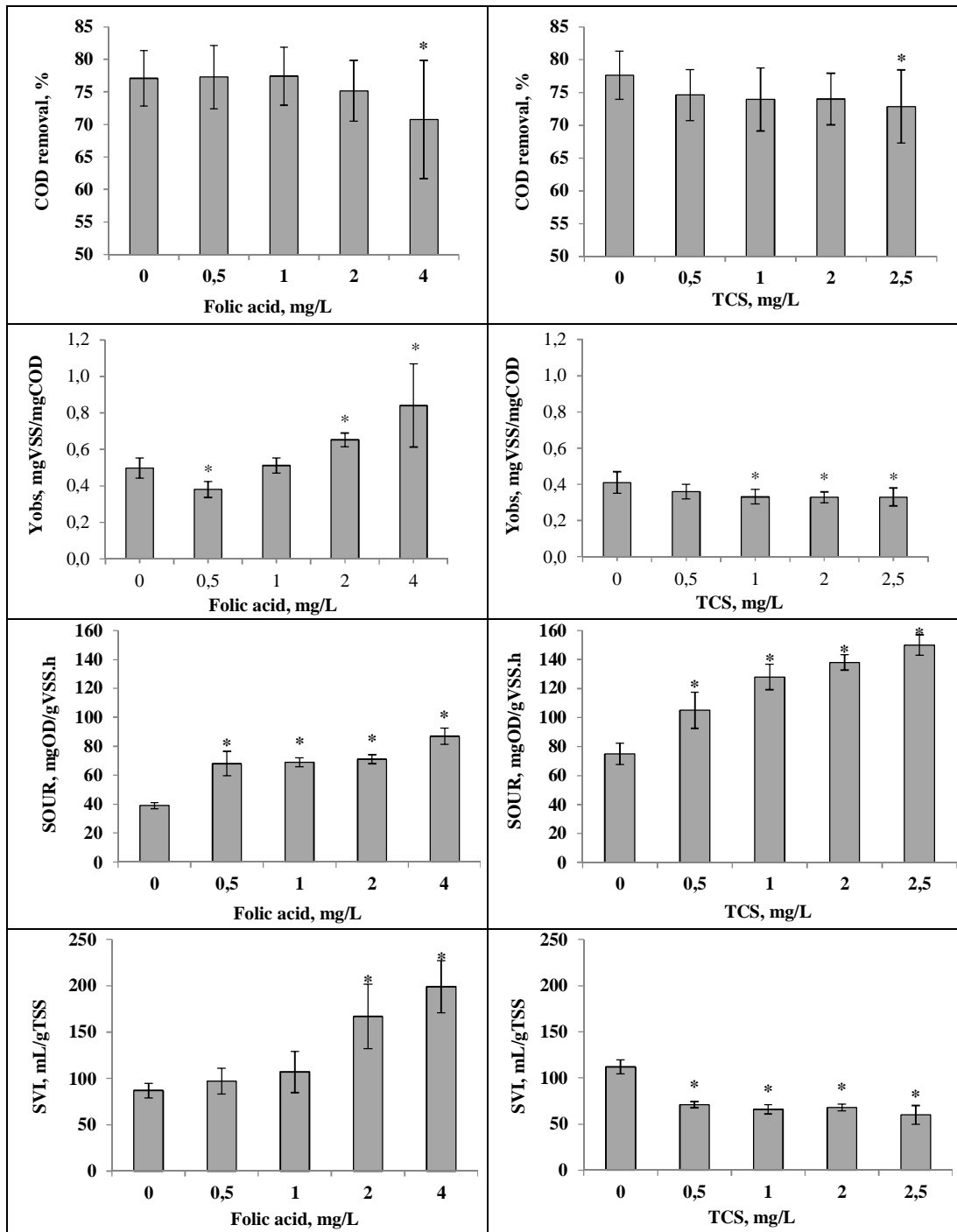


Figure 1. Effect of addition of folic acid or 3,3',4',5- tetrachlorosalicylanilide (TCS) on bleached eucalypt kraft pulp effluent treatment efficiency (COD removal), excess sludge production (Yobs), activity (specific oxygen uptake rate, SOUR) and quality (sludge volume index, SVI). (Average values \pm standard deviations). In each histogram, asterisks over bars indicate values that differ from the control ($p < 0.05$).

SOUR values were higher at all doses of folic acid and TCS than in controls. Increased SOUR values after folic acid addition have been reported in treatment of domestic (Torres and Vazoller, 2006) and recycled fiber mill effluents (Akerboom et al., 1994). These authors postulate that increased SOUR results from increased activity of metabolic pathways that are stimulated by folic acid. In the case of TCS, increased SOUR results from the attempt of microorganisms to satisfy their energy demands by increasing substrate degradation (respiration), as observed by various authors during treatment of domestic effluents (Chen et al., 2002; 2004; Liu and Tay, 2001).

Folic acid and TCS had opposite effects on SVI values. While doses of ≥ 2 mg/l folic acid increased SVI values, all doses of TCS evaluated decreased SVI and improved sludge settleability.

Based on the results of the preliminary studies, doses of 0.5 mg/L folic acid and 1.0 mg/L TCS were chosen for further evaluation, since these doses resulted in significantly lower sludge yields, without adversely affecting COD removal efficiency or sludge settleability. The chronic toxicity to the green alga *P. subcapitata* of the effluents treated with these doses of additives is presented Table 1. Effluents with additives presented higher toxicity after biological treatment than the control treatments. Toxicity of treated effluent after folic acid addition was even higher than primary effluent toxicity, an alarming result which may have been caused by folic acid itself or its effect on biological metabolism.

Table 1. Chronic toxicity (algal growth inhibition, IC_{25}) of bleached kraft pulp mill effluent before and after aerobic biological treatment with and without folic acid or 3,3',4',5-tetrachlorosalicylanilide (TCS).

Sample	Supplement	Dose, mg/L	IC_{25} , %	Toxic units
Primary effluent	-	-	22.1	4.5
	Folic acid	0	27.8	3.6
Biologically treated effluent		0.5	13.7	7.3
	TCS	0	44.0	2.3
		1.0	28.4	3.5

3.2. Effect of supplements under vary organic loading rates

The different organic loading rates evaluated in the second phase of this study are listed in Table 2. It is well known that one of the biggest challenges in treatment of pulp mill effluents is the large variations in their quality arising from variations in production processes (Rodrigues et al., 2010). Despite these variations, COD removal efficiencies remained relatively high and neither folic acid or TCS had a negative impact on them (Figure 2), confirming the results of the preliminary studies.

Table 2. Organic loading rates during different periods of biological treatment of bleached eucalypt kraft pulp mill effluent.

Period	Duration, d	Organic loading rate (g DQO.d ⁻¹)
1	14	2,1
2	10	3,5
3	14	7,2
4	10	4,2
5	12	1,8
6	10	3,8

Addition of either chemical resulted in significantly lower sludge yields (Yobs) than treatment with no additive during periods 3 to 6 (Figure 3). No differences among sludge yields were observed in the first two periods, corresponding to roughly two MCRTs, time apparently necessary for folic acid and TCS to exert their effects on sludge production. There was no evidence of sludge adaption to either folic acid or TCS, since reduced sludge production was maintained for 46 days. Hiraishi & Kawagishi (2002) observed that the positive effects of the uncoupler 4-nitrophenol waned after two weeks and were virtually eliminated after four weeks of treatment of domestic effluent.

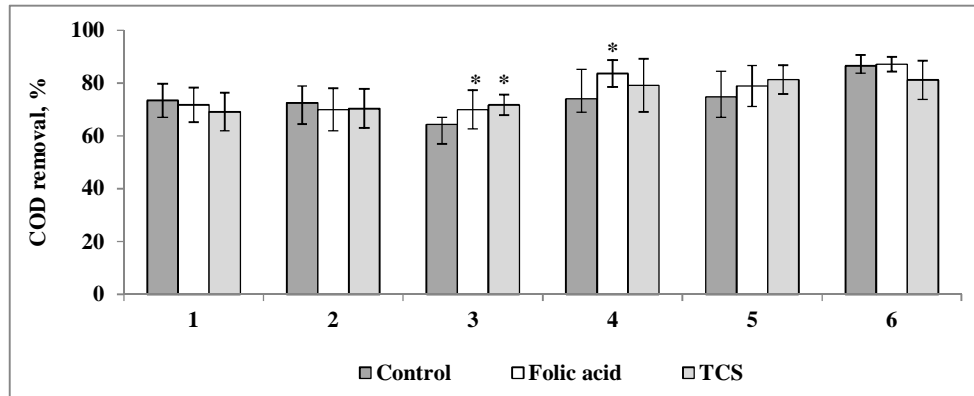


Figure 2. COD removal efficiency during aerobic biological treatment of bleached eucalypt kraft pulp mill effluent under varying organic loading rates, with and without addition of 0.5 mg/l folic acid or 1.0 mg/L 3,3',4',5-tetrachlorosalicylanilide (TCS). (Average values \pm standard deviations). In each treatment period, asterisks over bars indicate values that differ from the control ($p < 0.05$).

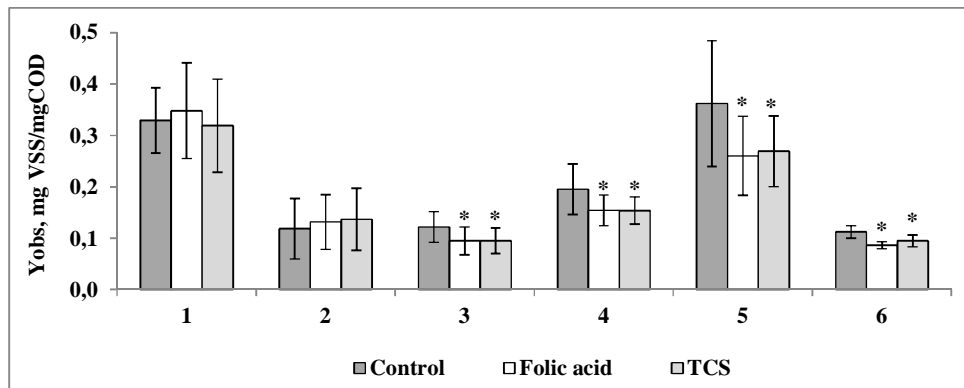


Figure 3. Observed sludge yield (Y_{obs}) during aerobic biological treatment of bleached eucalypt kraft pulp mill effluent under varying organic loading rates, with and without addition of 0.5 mg/L folic acid or 1.0 mg/L 3,3',4',5-tetrachlorosalicylanilide (TCS). (Average values \pm standard deviations). In each treatment period, asterisks over bars indicate values that differ from the control ($p < 0.05$).

SOUR and SVI values were only quantified during periods 5 and 6 (Figure 4). As observed in the preliminary studies, folic acid and TCS stimulated microbial activity, as expressed by increased SOUR values. Sludge settleability was not affected by either supplement, although in the preliminary study, 1.0 mg/L TCS reduced the SVI value over that of the control.

Toxicity was evaluated after the sixth treatment period (Table 3). Both supplements produced more toxic treated effluents than the control treatment. However, differently from the preliminary studies, TCS addition increased toxicity after treatment, while the control and folic acid treatments both reduced the toxic units of the primary effluent. However, a lower reduction in toxicity was found in the presence of folic acid than in the control treatment.

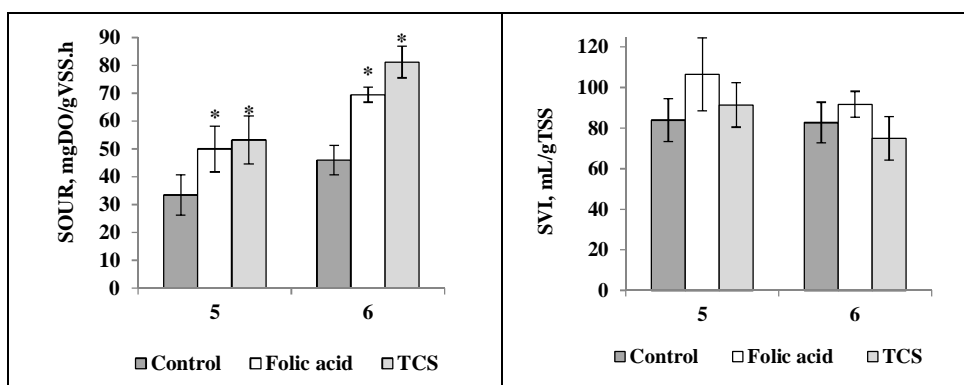


Figure 4. Sludge specific oxygen uptake rate (SOUR) and sludge volume index (SVI) during aerobic biological treatment of bleached eucalypt kraft pulp mill effluent under varying organic loading rates, with and without addition of 0.5 mg/L folic acid or 1.0 mg/L 3,3',4',5-tetrachlorosalicylanilide (TCS). (Average values \pm standard deviations). In each histogram, for each treatment period, asterisks over bars indicate values that differ from the control ($p < 0.05$).

Table 3. Chronic toxicity (algal growth inhibition, IC_{25}) of kraft pulp mill effluent before and after aerobic biological treatment of bleached eucalypt kraft pulp effluent with addition of 0.5 mg/L folic acid or 1.0 mg/L 3,3',4',5-tetrachlorosalicylanilide (TCS).

Sample		IC_{25} , %	Toxic units
Primary effluent		17.4	5.7
Biologically treated effluent	Control	57.6	1.7
	Folic acid	32.2	3.1
	TCS	15.4	6.5

4. CONCLUSIONS

Both folic acid (0.5 mg/L) and TCS (1.0 mg/L) proved capable of reducing excess sludge production in aerobic biological treatment of bleached eucalypt kraft pulp mill effluent without reducing COD removal efficiency. Both supplements, at the proper doses, maintained their positive effects under varying organic loading rates and had little effect on sludge settleability. However, sludge specific oxygen uptake rates and treated effluent chronic toxicity increased in the presence of both supplements. Effluent treatment plant managers must therefore evaluate aeration system capacity and degree of dilution in receiving waters when contemplating use of either supplement.

ACKNOWLEDGEMENTS

The authors thank CAPES and FAPEMIG for scholarship support and Lwarcel Celulose e Papel Ltda. for generously supplying effluent samples.

REFERENCES

- AKERBOOM, R.K.; LUTZ, P.; BERGER, H.F. Folic acid reduces the use of secondary treatment additives in treating effluent from paper recycling. In: International Environmental Conference – TAPPI Proceedings. 1994.
- APHA – AMERICAN PUBLIC HEALTH ASSOCIATION – Standard Methods for the Examination of Water and Effluent. Washington: APHA, AWWA, WEF. 22 ed., 2012.
- BRACELPA – Associação Brasileira de Celulose e Papel. Disponível em: <<http://www.bracelpa.org.br/bra2/?q=node/139>>. Acesso em julho de 2012.
- CHEN, G.-H., MO, H.-K., LIU, Y. Utilization of a metabolic uncoupler, 3,3',4',5-tetrachlorosalicylanilide (TCS) to reduce sludge growth in activated sludge culture. *Water Research*, v.36, n.8, p.2077-2083, 2002.
- CHEN, Y. X.; YE, F. X.; FENG, X. S. The use of 3,3,4,5-tetrachlorosalicylanilide as a chemical uncoupler to reduce activated sludge yield. *J. Chem. Technol. Biot.*, v. 79, p. 111–116, 2004.
- CHONG, N. –M.; WANG, C. –H.; HO, C. –H.; HWU, C. –S. Xenobiotic substrate reduces yield of activated sludge in a continuous flow system. *Bioresource Technology*, v. 102, p. 4069–4075, 2011.

- DEBELLEFONTAINE, H., PAUL, E. Reduction of excess sludge produced by biological treatment processes: effect of ozonation on biomass and on sludge. *Ozone Science and Engineering*, v.29, n.6, p.415-427, 2007.
- DUBÉ, E.; GAGNON, D.; LAVALLÉE, H.C.; ROBERT, S. Applications of folic acid in secondary effluent treatment. In: Environmental Conference. 2002. TAPPI
- ELVIRA, S. I. P.; DIEZ, P. N.; POLANCO, F. F. Sludge minimization technologies. *Reviews in Environmental Science and Bio/Technology*, v. 5, p. 375–398, 2006.
- GRADY JR., C.P.L.; DAIGGER, G.T.; LIM, H.C. *Biological effluent treatment*. 2ed., Nova Iorque: Marcel Dekker Inc., 1999.
- HIRAISHI, A.; KAWAGISHI, T. Effects of chemical uncouplers on microbial biomass production, metabolic activity, and community structure in a activated sludge system. *Microbes and Environments*, v. 17, n.4, p. 197-204, 2002.
- LAURENT, J.; JAZIRI, K.; GUIGNARD, R.; CASELLAS, M.; DAGOT, C. Comprehensive insight of the performances of excess sludge reduction by 90°C thermal treatment coupled with activated sludge at pilot scale: COD and N removal, bacterial populations, fate of heavy metals. *Process Biochemistry*, v. 46, p. 1808–1816, 2011.
- LIU, Y.; TAY, J. H. Strategy for minimization of excess sludge production from the activated sludge process. *Biotechnol. Adv.*, v. 19, n. 2, p. 97–107, 2001.
- LOW, E. W., CHASE, H.A., MILNER, M.G., CURTIS, T.P. Uncoupling of metabolism to reduce biomass production in the activated sludge process. *Water Research*, v.34, n.12, p.3204-3212, 2000.
- MAYHEW, M.; STEPHENSON, T. Biomass yield reduction: is biochemical manipulation possible without affecting activated sludge process efficiency?. *Water Sci. Technol.*, v. 38, p.137–144, 1998.
- METCALF & EDDY. *Effluent engineering: treatment and reuse*, 4 ed. Boston: McGraw-Hill, 2003.
- OSTRANDER, S.J. A non-conventional solution to an old problem. *Operations Forum*, v. 9, n. 1, 1992.
- RHO, S.; NAM, G.; SHIN, J.; JAHNG, D. Effect of 3,3',4',5-Tetrachlorosalicylanilide on Reduction of Excess Sludge and Nitrogen Removal in Biological Effluent Treatment Process. *J. Microbiol. Biotechnol.*, v. 17, n. 7, p. 1183-1190, 2007.
- RODRIGUES, C.L.S.; MOUNTEER, A H.; STOPPA, T.V.; DALVI, L.C. Chemical components of bleached eucalypt kraft pulp effluent COD and treatment removal efficiency during normal mill operation and maintenance shutdowns. *Wat. Sci. Technol.*, v.62, n.7, p.1567-1573, 2010.
- SABY, S., DJAFER, M., CHEN, G.-H. Effect of low ORP in anoxic sludge zone on excess sludge production oxic-settling-anoxic activated sludge process. *Water Research*, v.37, n.11, p.11-20, 2003.
- STRUNKHEIDE, J. *Stabilized folic acid vitamin for the reduction excess sludge in sewage treatment plants*. Disponível em: <<http://www.dosfolat.de/literature/WWWT-paper-2004.pdf>>. Acesso em julho de 2012.
- TAKDASTAN, A.; MEHRDADI, N.; AZIMI, A. A.; TORABIAN, A.; NABI BIDHENDI, G. Investigation of intermittent chlorination system in biological excess sludge reduction by sequencing batch reactors. *Iran. J. Environ. Health. Sci. Eng.*, v.6, n.1, p.53-60, 2009.
- TORRES, D. P. C.; VAZOLLER, R.F. Avaliação da influência da adição de ácido fólico na microbiota de lodos ativados através de bioensaios de respirometria. In: XXX CONGRESSO INTERAMERICANO DE INGENIERÍA SANITARIA Y AMBIENTAL. . *Anais...* Punta del Este, Uruguai, 2006.
- USEPA – United States Environmental Protection Agency. Method 1683 - *Specific oxygen uptake rate*, EPA-821-R-01-014, Washington, 2001.
- WANG, G.; SUI, J.; SHEN, H.; LIANG, S.; HE, X.; ZHANG, M.; XIE, Y.; LI, L.; HU, Y. Reduction of excess sludge production in sequencing batch reactor through incorporation of chlorine dioxide oxidation. *Journal of Hazardous Materials*, v. 192, p. 93-98, 2011.
- YAN, S.; MIYANAGA, K.; XING, X.; TANJI, Y. Succession of bacterial community and enzymatic activities of activated sludge by heat-treatment for reduction of excess sludge. *Biochemical Engineering Journal*, v.39, p.598–603, 2008.
- YONGDE, L.; JUN, L.; JIHONG, Z. Factors Analysis on Ultrasonic Sludge Reduction in Continuous Flow System. 3rd INTERNATIONAL CONFERENCE ON BIOINFORMATICS AND BIOMEDICAL ENGINEERING. *Proceedings...* Beijing, China, 2009.