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Alkaline Pretreatment of Kraft Mill Sludge to Improve Its Anaerobic Digestion

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Aerobic processes are the most common technologies used in wastewater treatment plants, particularly in the pulp and paper industry. The activated sludge process presents a high biological oxygen demand (BOD_5) removal efficiency (between 85 and 95%) (Diez et al. 2001), but generates 0.5 kg dry weight excess sludge/kg BOD_5 (Winkler 1986). This excess sludge must be treated for stabilization and mineralization of the organic matter present (Llagostera et al. 1997).

Currently, there are three main options for controlled disposal of biological sludge: landfilling, incineration and agricultural or forest land use (Matthews 1998). On one hand, incineration is still a very expensive process because of the high water content of the raw sludge (Jokela et al. 1997), and on the other hand, this high water content is becoming a restriction in modern landfills. So, the tendency is to increase solids content of the sludge with a dewatering process like a filterpress, followed by an anaerobic digestion process. This anaerobic stage mainly reduces the sludge volume, degrades putrescible organic matter, recovers energy and a stabilized solid rich in nutrients (Jokela et al. 1997). This anaerobic sludge digestion has the disadvantage that it is a very slow process (20-30 days) and requires large equipment, because of the complex reaction mechanisms involved. In fact, Eastman and Ferguson (1981) determined that hydrolysis and sludge solubilization are the controlling steps in the anaerobic sludge digestion. In general, pulp and paper mill secondary sludge is constituted principally of biomass, cellulose and slowly biodegradable compounds like lignin. Protein content varies between 22 and 55%, lignin between 20 and 58%, carbohydrates are between 0 and 23%, lipids between 2 and 10% and cellulose between 2 and 8% (Kyllonen 1986). The cell walls (of the microorganisms present in the biomass) behave as a physicochemical barrier to exoenzyme degradation and hydrolysis (Kunz 1992), limiting the global efficiency of the digestion process (Dichtl 1996). Based on this, the availability of intracellular organic material from the biomass is restricted and the total organic solids biodegradation cannot be maximized within adequate retention times further than a given limit (around 55% for domestic sewage sludge) (Baier and Schmidheiny 1997).

One chemical method that has been investigated for the sludge solubilzation

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process is the use of an alkaline treatment with sodium hydroxide (NaOH) compared with lime. Results for NaOH have been found to be better (Rajan et al. 1989) with values of soluble chemical oxygen demand (COD)/total COD between 28 and 42% for 1% total solids sludge, with retention times between 12 and 24 h (Chiu et al. 1997). Coupling this alkaline process with a thermal rise, it is possible to greatly improve sludge organic matter solubilization. In fact, for a 1% total solids sludge thermochemical treatment at 175°C in presence of NaOH, maximum values of around 68% soluble COD/total COD were reached in 24 h (Haug et al. 1978). On the other side, for a 4.3% total solids sludge, values of soluble COD/total COD around 55% were obtained under the same conditions (Stuckey and McCarty 1978).

Based on this, the main objective of this work is to study the alkaline pretreatment of the excess sludge produced in the aerobic Kraft mill wastewater treatment process, for further enhancement of anaerobic digestion.

MATERIALS AND METHODS

Wastewater from a modern bleached Kraft mill located in the south of Chile was sampled and analyzed. This mill produces two types of pulp: Standard, with four steps (D/C EO D_1 D_2) for bleaching softwood pulp with 50% chlorine-dioxide substitution in step one, and Elemental Chlorine-Free (ECF) pulp (Do EOP D_1 D_2). D and C denotes ClO_2 and Cl_2 bleaching stage, respectively, EO indicates oxygen-reinforced alkaline extraction stage and EOP denotes oxygen and hydrogen-peroxide reinforced alkaline extraction stage. Inside the mill, the wastewater receives primary treatment in a settling tank to reduce fiber and suspended solids. The samples used corresponded to the global untreated wastewater after primary sedimentation process and were taken periodically (approximately once a month) throughout a one-year period. Samples were cooled for one day and analyzed immediately for physical and chemical characteristics that are shown in Table 1.

On one side, it is important to note that the BOD_5/COD ratio is 0.26, which means that there is an important slowly biodegradable organic compounds fraction in the effluent, composed mainly by tannins, lignin and phenolic compounds. On the other side, under aerobic conditions BOD_5 removal efficiencies for this effluent move between 85 and 95%, while COD removal efficiencies move normally between 46 and 60% for hydraulic residence times (HRT) > 6 h (Diez et al. 2001). Additionally, aerobic bacteria do not remove color and phenolic compounds are poorly degraded. This is a very important factor to take into account while analyzing the secondary sludge characterization and alkaline hydrolysis.

Excess industrial secondary sludge from the aerobic Kraft mill effluent treatment plant has been used for characterization (Table 2) and for kinetic studies during alkaline hydrolysis assays. The total COD value of 14,100 mg/L is a very large

quantity in this case, compared with municipal sewage sludge total COD that moves between 7,000 and 9,000 mg/L (Chiu et al. 1997). This means that the secondary Kraft mill sludge should include the slowly biodegradable compounds and the biomass itself. Moreover, the soluble COD value of 1046 mg/L gives a soluble COD/total COD initial ratio of 7.4%, which is two times higher than a normal ratio for municipal sewage sludge.
The high variability in the composition of the untreated wastewater (Table 1) could be a result of the different products and bleaching alternative processes used in the plant. On the other hand, the wastewater treatment plant acts as a "buffer", producing a sludge with a lower composition variability (Table 2).

Table 1. Untreated wastewater characterization

Parameter	Unit	Untreated wastewater*		
		Range	Average	Std. Deviation
pH		3.5-10.6	5.1	2.3
Color	U Pt/Co	592-1400	951	246
BOD_5[1]	mg/L	242-513	318	93
COD[2]	mg/L	823-1942	1208	424
Phenolic Compounds UV_{215}	mg/L	190-350	322	47
Tannin-lignin	mg/L	44-64	52	6

*Values are the average of eleven determinations
[1] BOD_5: Biological oxygen demand
[2] COD: Chemical oxygen demand

Table 2. Kraft mill secondary sludge characterization

Parameter	Range*	Average	Std. Deviation
pH	7.01-7.21	7.11	0.05
Total Solids (TS) %	1.20-1.28	1.24	0.02
Total COD mg/L[1]	13,700-14,500	14,100	230
Soluble COD mg/L	1,025-1,067	1,046	11
Total Susp. Solids (TSS) mg/L	9,210-9,820	9,520	172
Volatile Susp. Solids (VSS) mg/L	7,160-7,780	7,470	170
Humidity %	91.0-91.7	91.4	0.2
Organic Matter %	62.1-66.4	64.3	1.1

* Total of five samples
[1] COD: Chemical oxygen demand

The sludge solubilizaton effect of NaOH and potassium hydroxide (KOH) was studied in a 2.0 L batch mixed reactor for kinetic purposes. From the original five samples, only one was used for this purposes. The same sample was split and used for hydrolysis parameters determination. NaOH and KOH doses moved between 20 and 200 meq/L and samples were taken during the alkaline reaction with sludge as described by Haug et al. (1978) and Chiu et al. (1997). Soluble COD, protein and volatile suspended solids (VSS) were taken as variables for optimal chemical dose determination. All evaluated parameters were determined according to standard methods (APHA-AWWA 1989).

RESULTS AND DISCUSSION

Alkaline hydrolysis results are shown in Figure 1 for soluble COD/total COD increase in the supernatant liquid after 24 h hydrolysis. Initial soluble COD/total COD value of the sludge was 7.4% and maximum values of around 32 % were observed for the alkaline reactive doses starting from 80 meq/L. So, for a 14,100 mg/L total COD sludge, soluble COD moved from 1,046 to around 4,500 mg/L. This could mean, considering that the secondary Kraft mill sludge contains slowly biodegradable compounds and biomass, that the alkaline hydrolysis would hydrolyze preferentially the organic compounds, because it is difficult to break the microorganisms cells. On the other hand, values of soluble COD/total COD ratio for alkaline hydrolysis are according to previous results for municipal sewage sludge. In fact, this ratio can move between 20 and 81% after different chemical and physical pretreatment (Chiu at al. 1997). Also, there is no significant difference between NaOH and KOH as supposed, and 60 meq/L appears to be the optimum alkaline reactive dose.

The pH increase was also measured during 24 h hydrolysis. Starting from initial pH of 7.21 in the sludge, a final pH of around 13.2 was obtained for the maximum alkaline reactive dose after 24 h hydrolysis. This is an important parameter to take in account for further anaerobic digestion or for supernatant recirculation to the aerobic stage. In fact, considering a supernatant recirculation stream, it should be very useful for acid wastewater neutralization.

Soluble protein increase in the sludge supernatant was also determined in hydrolysis assays. It was observed that the initial soluble protein concentration of 91 mg/L rose to 529 mg/L for a 60 meq/L dose of NaOH. For maximum alkaline doses, the soluble protein value reached 693 mg/L for NaOH, with an increase of 7.6 times the original concentration (Figure 2).

Finally, a 21% decrease in volatile suspended solids (VSS) concentration (i. e., from 7.6 to 6.0 g/L) was observed after 24 h hydrolysis with a 60 meq/L dose of NaOH (Figure 3).

Kinetics were also determined for soluble COD. As proposed by Lin and Chang (1995) for municipal sewage sludge, we fit the polynomial expression to the experimental points following:

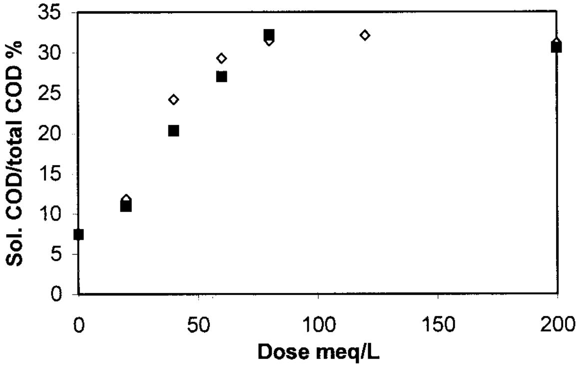

Figure 1. Sludge soluble chemical oxygen demand (COD)/total COD increase with alkaline hydrolysis ◊sodium hydroxide (NaOH) ■potassium hydroxide (KOH)

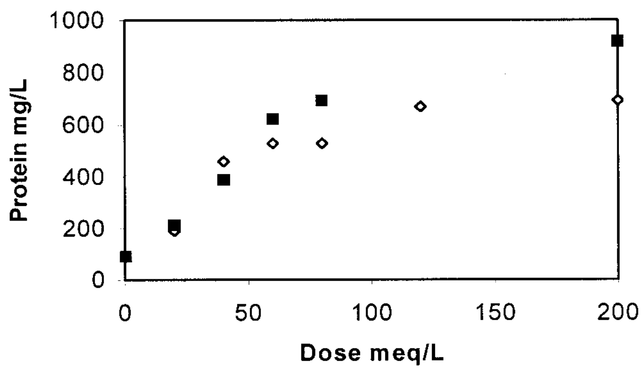

Figure 2. Sludge protein increase with alkaline hydrolysis ◊sodium hydroxide (NaOH) ■potassium hydroxide (KOH)

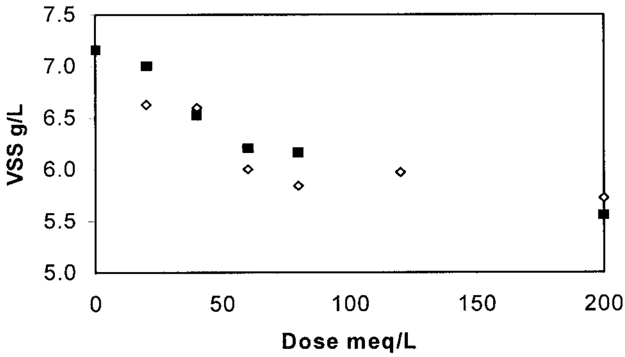

Figure 3. Sludge volatile suspended solids (VSS) decrease with alkaline hydrolysis ◊sodium hydroxide (NaOH) ■potassium hydroxide (KOH)

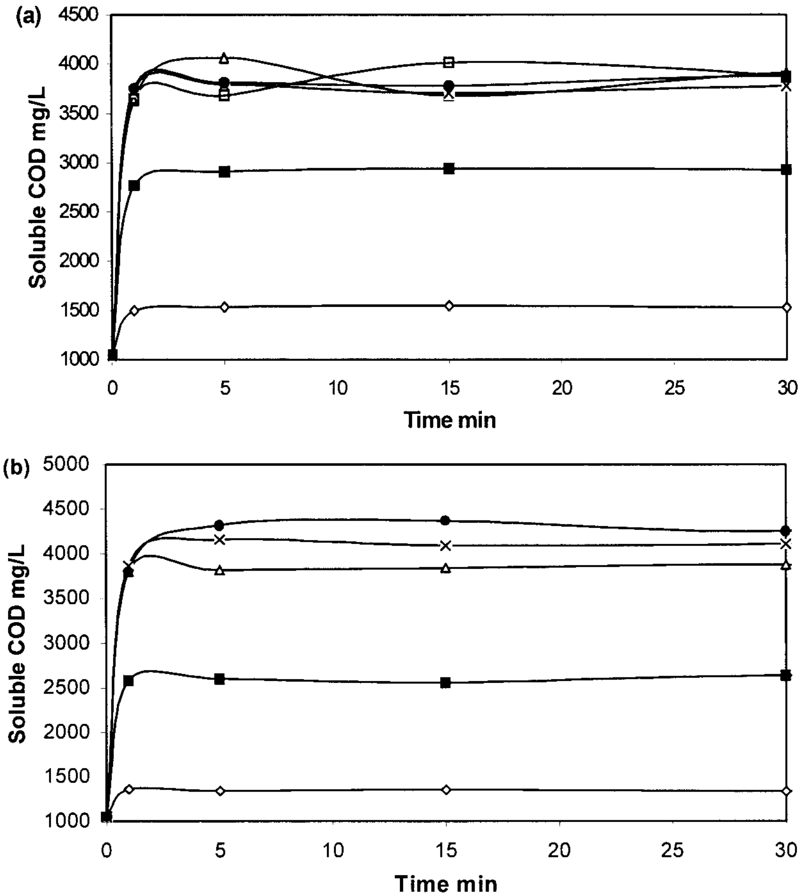

Figure 4. Sludge soluble chemical oxygen demand (COD) kinetics for (a) sodium hydroxide (NaOH) and (b) potassium hydroxide (KOH), ◊20 ■40 Δ60 x80 □120 ●200 meq/L alkaline reactive dose

$$C = k_0 + k_1 * t + k_2 * t^2 + k_3 * t^3$$

With C: soluble COD, t: hydrolysis time and k_0, k_1, k_2 and k_3: constants. The derivation of this equation leads to:

$$dC/dt = k_1 + k_2 * t + k_3 * t^2$$

If we assume "t" approaching zero, we can obtain the initial hydrolysis rate (k_1) for all alkaline doses in Kraft mill sludge. As shown in Figure 4, taking the initial 30 min of hydrolysis (the results do not show any significant changes after this time until 24 h), the initial hydrolysis rates for the different alkaline doses can be obtained (Table 3). Sixty meq/L was determined to be the optimum dose for sludge solubilization. This is because for KOH, the k_1 increase between 60 and

80 meq/L is only 15% compared with the previous increase of 76% between 40 and 60 meq/L dose. Besides, 60 meq/L NaOH is clearly the optimum dose for the k_I value.

Table 3. Initial sludge hydrolysis rate k_I as soluble chemical oxygen demand (COD) for sodium hydroxide (NaOH) and potassium hydroxide (KOH)

Dose meq/L	NaOH		KOH	
	k_I mg/L min	R^2	k_I mg/L min	R^2
20	127.4	0.67	73.7	0.54
40	484.1	0.67	405.7	0.61
60	828.3	0.71	713.9	0.61
80	718.2	0.62	823.2	0.68
120	659.3	0.65	-	-
200	717.6	0.62	869.9	0.74

In general, it can be concluded that for an alkaline pretreatment of the Kraft mill sludge with NaOH or KOH, it its possible to obtain up to a 32% increase in the soluble COD/totalCOD ratio which will probably improve the methane yield and the efficiency of the anaerobic digestion process. Moreover, the pretreatment process will help to reduce the final sludge solid volume after anaerobic fermentation, resulting in less impact to the environment and increasing the lifetime of landfills. Considering that in the future agricultural or forestland use of the digested Kraft mill sludge should be one of the principal safe disposal techniques because of the expensive costs to send it to a commercial landfill (Phillips et al. 1997), it will be possible to choose between NaOH or KOH depending on soil salt composition. Besides, characterization results indicate that the heavy metals content of the dry Kraft mill secondary sludge (Pb, Cu, Zn, Cd, Ni and Hg) do not surpass the European Economic Community Directive 86/278-EEC for each metal (data not shown), which indicates that safe agricultural use could be possible in the future.

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