한국환경위생학회지, 제24권 제1호 (1998)
Kor. J. Env. Hlth. Soc., Vol. 24, No. 1, pp 70~79 (1998)

The Anaerobic Biodegradability and Methanogenic Toxicity of Pulping Wastewaters

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펄프폐수의 혐기성 생분해능 및 메탄 생성균의 독성에 관한 연구

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국문초록

본 실험의 목적은 다양한 펄프제조 조건과 여러 형태의 리그노 셀루로우스 성분이 펄프폐수의 혐기성 생분해에 미치는 영향을 규명하는 것이다. 실험에 사용된 폐수는 일반적으로 펄프 제조시에 발생되는 폐수를 대상으로 하였으며, 펄프제조(pulping conditions) 조건은 TMP공정과 소다 펄프공정을 적용하였다. 혐기성 생분해 가능성 시험 및 독성실험은 35±2℃의 중온상태에서 입상슬러지를 식종물질로 사용한 회분식 반응조를 이용하였다. TMP공정의 배출되는 폐수는 산으로의 전환율이 총 COD기준으로 68~87%로 매우 높은 혐기성 생분해 가능성을 보였다. 그리고 TMP공정폐수는 일반적으로 제지폐수 처리시 독성농도라고 알려진 농도에서도 메탄생성균에 독성을 주지 않았고, 또한 COD 10 g/*l*의 농도에서도 처리에 저해가 일어나지 않았다. 반면에, 알카리성 상태에서 준비된 펄프폐수의 경우는 생분해성이 매우 낮아서 대략 50%정도의 산전환율을 보였으며, 메탄생성균에 상당한 저해를 주었다. 메탄생성균의 활성도에 50%저해를 주는 농도는 2.1~5.4 gCOD/*l*였다. 알카리성 펄프폐수의 독성에 대한 추가 실험결과 펄프내 wood resin이 산이나 중성 pH 부근에서는 잘 용해가 되지 않고 알카리성 상태에서 쉽게 용해되어 메탄생성균에 저해를 나타내는 것으로 밝혀졌다. 따라서 펄프제조시 나무성분이 알카리성분과 접촉할 경우 후속하는 혐기성 처리공정의 메탄생성균에 심각한 저해를 줄 수 있다.

Keywords : Anaerobic biodegradability, Methanogenic toxicity, Pulping wastewater

I. Introduction

The forest industry utilizes wood and other lignocellulosic feedstocks as raw materials for production of paper. The major constituents of wood are cellulose, hemicellulose, lignin and resin. Softwoods, hardwoods and straw have different proportions of chemical components as shown in Table 1.[1,2]

The processing of wood in paper mills involves various operations including debarking, pulping and bleaching that result in the discharge of highly polluted wastewaters. The quantity and types of pollutants in these effluents vary with the type of lignocellulosic feedstock used as raw material, the process conditions applied(pH, temperature, pressure, chemical and mechanical treatment) and the specific water consumption.[3] High pressure and temperature and particularly chemical addition result in an increased release of organic matter into the process water and extensive lignin solubilization. Therefore, the pollution loads and the color due to dissolved lignin compounds is very high for chemical as compared to mechanical pulping effluents. The COD loads associated with mechanical pulping process range from 20-50 kg COD per ton of pulp[4] whereas those corresponding to soda pulping process may be as high as 500-900 kgCOD per ton of pulp. Nevertheless, the black liquors ori-

Table 1. Literature averaged composition of hardwoods, softwoods and straw

Constituent	Composition(% total dry weight)		
	Harwood	Softwood	Straw
Lignin	17~26	25~32	17~19
Hemicellulose	22~34	15~18	27~32
Cellulose	58~64	55~61	33~38
Extractives	3~8[a]		1~2[b]
Mineral matter	1		6~8

[a] Alcohol-benzene extract followed by hot water extraction.
[b] Ether extract.

ginating from kraft and soda processes are usually burnt to recover the pulping chemicals and the calorific power from the organic components, diminishing to a great extent the environmental impact associated with these pulping processes. Conventional recovery processes are not economically viable in small paper mills and in those using non-woody raw materials with a high silica content.[5] Black liquors represent a very important pollution source in several countries where small scale mills are common.[5]

Pulp and paper mill effluents can cause considerable damage to receiving waters if discharged untreated. The environmental impact associated with these wastewaters is not only restricted to the oxygen demand, but also numerous effluents from the forest industry display acute toxicity to fish and other aquatic organism.[6] Furthermore, these wastewaters streams often exert inhibitory effects to microorganism that can disturb biological treatment systems.[7] Aerobic treatment systems have traditionally been supplied for reducing the pollution caused by the pulp and paper industry effluents. However, in the last years, the rising energy prices and the relatively high operation costs of conventional aerobic wastewater treatment technologies. Non-inhibitory forest industry wastewaters rich in readily biodegradable organic matter such as paper recycling wastewaters, mechanical pulping effluents and sulfite evaporator condensates are successfully treated in full-scale anaerobic reactors.[8] However, the number of full scale applications to toxic and more complex forest industry wastewaters is still very limited. An evaluation of the factors determining the composition of paper mill wastewaters, such as the lignocellulosic feedstock used and the conditions applied during pulping or bleaching, as well as a good understanding of the fate of the wastewater components in anaerobic system is necessary to determine the potential and limitations of the anaerobic technologies for the treatment of these toxic wastewater streams.

The purpose of this study was to evaluate the effect of mechanical and soda pulping processes on the anaerobic treatability of pulping wastewaters originating from various lignocellulosic feedstocks.

II. Materials and Methods

1. Preparation of wood and straw pulping wastewaters

Extracts were prepared from lignocellulosic feedstock commonly used in the forest industry, namely, pine, spruce and birch wood, and wheat straw. Birch wood samples were collected in a local forest from birch logs that were recently cut. Spruce and pine chips were obtained from a D paper factory. Wheat straw was purchased in a local shop. The pulping conditions used were representative of those applied in thermomechanical pulping(TMP) and soda pulping processes. Prior to pulping, debarked wood chip samples and straw were air dried at 70℃ for 48 hours and ground in a cross mill. A slurry containing 100 g of ground wood or straw per liter of water was cooked at 120℃ for 2 hours. When soda pulp waters were prepared 8 g NaOH were also added. The remaining pulp was separated from the pulp waster by centrifugation and subsequent filtration. Finally, the pulp waters were neutralized by addition of NaOH of HCl, as required, and stored in refrigerated container.

2. Treatment of the pulping wastewaters

(1) Ether extraction

Resin was extracted from the pulping wastewater by liquid-liquid extraction with diethyl ether under strongly acidic(pH 2-3) conditions.[9] The

sample was extracted three successive times with an equal volume of ether(50:25:25% of the total ether volume in the 1st:2nd:3rd extraction). The aqueous fraction was partially evaporated in a rotary evaporator to remove traces of ether. The required volume of water was added to reach the initial sample volume, and solution was neutralized with NaOH.

(2) XAD treatment

1 *l* of the pulping wastewater(5 to 10 gCOD/*l*) at pH 9 was shaken with 71.5 g of a polymeric resin(XAD-2) for 5 hours. Subsequently, the sample was paper filtered and neutralized with HCl.

(3) Ca^{2+} precipitation

1 *l* of the pulping wastewater(5 to 10 gCOD/*l*) was treated at pH 11 with 1,000 mg/*l* of Ca^{2+}, supplied as $CaCl_2 \cdot 2H_2O$. Precipitation was allowed to occur overnight after which the wastewater was paper filtered and neutralized with HCl.

(3) PVP treatment

Pulping wastewaters were treated with an insoluble polyamide, polyvinylpyrolidone (PVP), to specifically remove the fraction with tannic qualities. The treatment was in accordance with the method described by Field et al. (14.3 PVP/*l* for 1 hour shaking followed by filtering the wastewater).[10]

(4) Acid precipitation

1 *l* of the wastewater(5 to 10 g COD/*l*) was adjusted to pH 2 with HCl. The precipitation was allowed to occur overnight. The pulp wastewater was centrifuged and the precipitate and filtrate quantitatively recovered. The precipitate was repeatedly washed with a dilute HCl solution(pH 2) to removed traces of the mother liquid, centrifuged and suspended in 1 *l* of H_2O. Finally, the filtrate and suspended precipitate were neutralized.

3. Analyses

Samples for COD and volatile fatty acid(VFA) determination were filtered. COD, TSS and VSS were determined according to Standard Methods.[11] The pH was determined with Orion 920 pH-meter immediately after sampling in order to avoid a pH rise due to the loss of carbon dioxide from the liquid. VFA were analyzed by gas chromatography using a Hewlett-Packard model 5890 equipped with a HP-FFAP capillary column.

Carbohydrate content in the wood extracts was determined colorimetrically at 480 nm by the sulfuric-phenol method,[12] using analytical grade glucose as a standard. The ultraviolet absorbance at 280 nm was determined in a 1 cm quartz cuvette by diluting the samples to less than 0.8 absorbance units in a 0.02 M borate buffer, providing a pH of 9.1. The lignin content in the analyzed samples was estimated from the ultraviolet spectrophotometer at 280 nm using an absorptivity coefficient of 22.3 *l* per g per cm.[13] This spectrophotometer method is based on the distinct absorption of the aromatic ring at 280 nm.[14] It should be noted that other liquor components, especially aromatic extractives, also absorb light at this wavelength. Resin content in wood was determined by extraction of a known amount of the wood sawdust with a cyclohexane: methanol(2:1 in v/v%) solution in a Soxlet apparatus for 8 hours, and subsequent gravimetric determination of the amount of wood resin after drying the residue at 105℃.

4. Chemicals and Biomass

The chemicals used were purchased from Merk. The yeast-extract was supplied by Gist-Brocades. Amberlite XAD-2 and PVP were purchased from the Janssed chemica.

The granular sludge used in these experiments was obtained from a full scale UASB reactor treating distillery wastewater. The sludges were elutriated to remove the fines and stored at 4℃ under nitrogen gas. The sludge used was not acclimated to the pulping wastewater prior to the toxicity assays.

5. Biological Assays

All assays contained macronutrients and trace elements required for bacterial growth. Batch fed assays were conducted in 0.6 or 1.2 *l* glass serum flasks sealed with a rubber septum and a screw cap. The assay medium was flushed with nitrogen gas prior to incubation of the serum vials in a temperature controlled room at 30±2℃. The serum flasks were not shaken during the as-

say period. Methane production was monitored periodically during the assay with modified Mariotte flask. This flasks were filled with a 3% NaOH solution which served to remove the CO_2 contained in the biogas

(1) Anaerobic toxicity assay

In this study, two types of toxicity experiments were conducted as outlined follows :

1) Type A

This method used to determine the methanogenic toxicity of soda pulping liquors. The assays were carried out in two consecutive feedings. In the first feeding, tap water, granular sludge(1.5 gVSS/*l*) and known amounts of wastewater COD were transferred to the serum flasks containing nutrient solution. No wastewater was added to the substrate controls. Subsequently, distilled water was added to completed a medium volume of 0.1 *l* and, afterwards, the substrate controls and treatments(assays containing wastewater) were supplied with 4 gCOD/*l* of a neutralized volatile fatty acid(VFA) solution. The composition of the VFA solution that served as substrate was 100:100:100 g acetate:propionate:butyrate per kg. Finally, 1g $NaHCO_3$ per gram of biodegradable wastewater COD was added to the treatment containing the highest assay concentration to buffer eventual accumulation of VFA. The same quantity of $NaHCO_3$ was also supplied to the other treatment and to the substrate controls. On day 14, all serum flasks were provided with a second substrate feeding in order to evaluate the residual activity of the sludge after exposure to the pulp wastewater. The supernatants were carefully decanted to avoid losses of methanogenic sludge and replaced, while maintaining nitrogen gas flushing in the headspace, with a nutrient supplemented medium containing 4 gVFA-COD/*l*. No wastewater was included in the replacement medium. Finally, the serum flasks were incubated for 1 to 2 weeks.

2) Type 2

This method was applied to assay the methanogenic toxicity of TMP wastewater at concentrations ranging 5 to 20 g COD/*l*. The method described in assay type A is not reliable for determination the methanogenic toxicity when the wastewater provides a high concentration of substrate to the medium. The large differences in the VFA concentration of the various treatment complicate the comparison of the treatment activities with that of a single substrate control. During the first feeding each treatment was paired with a corresponding substrate control which contained an equal concentration of biodegradable COD supplied as VFA. The composition in COD basis of the neutralized VFA stock solution utilized in the substrate controls was 75:20:5 acetate:propionate:butyrate, similar to that of the completely acidified wastewater. The treatments were not supplied with VFA as the wastewater itself provided the substrate for the toxicity assay. To buffer eventual accumulations of VFA, 1g $NaHCO_3$ per gram of biodegradable COD was added to the treatment. The second feeding was the same as previously described in the toxicity assay type A.

The specific methanogenic activity, expressed as the amount of CH_4 produced by 1 g of sludge VSS per day(gCH_4-COD per g VSS per day), was calculated in all toxicity assays from the slope of the methane production versus time curve and the quantity of VSS. The methanogenic activities in the first and second feeding for each concentration point were calculated in the time interval corresponding to the maximum control activity. The inhibited activity was expressed as percentage of the control activity, and it is abbreviated as (% ACT). The percentage inhibition (% I) is defined as : % I=100 − % ACT. The wastewater concentration that caused 50% and 80% inhibition of the methanogenic activity is referred to as 50%I and 80% IC, respectively. It should be noted that the first feeding is usually less reliable than the second assay feeding. This is due to the different rates and levels of acidification in the treatments and their respective controls and the fact that the toxins often do not fully express their inhibiting activity prior to the time period used to calculate the methanogenic inhibition in the first feeding.

(2) Detoxification experiments

The detoxification obtained by detectively removing specific wastewater components was evaluated in anaerobic toxicity assays fed the ori-

ginal and treated pulping wastewater, following the procedure previously described in the toxicity assay type A. A concentration close to the 50% IC was chosen as a standard concentration for the detoxification experiments.

(3) Anaerobic biodegradability

The biodegradability experiments were conducted in 0.6 *l* flasks. Granular sludge(5 gVSS/*l*), distilled water and a known amount of wastewater COD were transferred to the flasks containing 0.1 *l* of the nutrient solution. The assay COD concentration after dilution to the final volume(0.5 *l*) ranged from 5 to 5 gCOD/*l*. The biodegradability assays of the soda pulp wastewater were supplied with a lower substrate concentration approximately 2 g COD/*l* to minimize methanogenic inhibition during the assays. The latter experiments were conducted in 1.2 *l* serum flasks to allow a more accurate determination of the methane production. All experiments included a sludge blank lacking substrate. The treatment and blanks were supplied with 1 g $NaHCO_3$ per gram of biodegradable COD. The percentage acidification of the wastewater COD was calculated by the sum of the cumulative CH_4-COD and the media VFA-COD for a given assay period. The acidification results reported are correlated for the acidification of the sludge controls.

III. Results

The average composition of the wood and straw pulping wastewaters used in this study and the yield of the soluble organic matter from the various lignocellulosic feedstocks are listed in Table 2.

Autoclaving the aqueous wood slurry(120℃, 2h) at the natural wood pH resulted in yellow colored, weakly acidic(pH 4.7) pulping wastewaters of intermediated COD strength(3 to 5 g COD/*l*). The amount of the lignocellulosic material dissolved after pulping ranged from 33 to 42 gCOD per kg of dried wood. Soda pulp liquors, on other hand, were dark brown colored and contained high concentrations of dissolved organic matter(20 to 40g COD/*l*). The organic matter dissolved in the alkaline liquors ranged from 187 to 384 g COD per kg of dried wood or straw, which are values that are significantly higher than those observed for the TMP wastewater.

Table 3. The average acidification of the wastewater COD during batch anaerobic digestion of pulping wastewaters(the acidification data reported were determined on the 15th day of the assay)

Pulping method	Lignocellulosic material	Acidification(%)
TMP	Pine	78.4
	Spruce	79.8
	Birch	86.5
	Straw	67.5
Soda	Pine	50.6
	Spruce	46.7
	Birch	67.3
	Straw	45.4

Table 2. The average composition of the wood and straw pulping wastewater used in this study and the yield of soluble organic matter from the various lignocellulosic feedstocks

Component % COD	Pulping method and lignocellulosic feedstock[a]							
	TMP				Soda			
	P	S	B	St	P	S	B	St
VFA	1	2	6	5	8	12	28	10
Alcohol[b]	ND	ND	ND	ND	0	0	0	0
Sugar	ND	ND	ND	ND	11	12	ND	35
Lignin	20	16	ND	32	40	46	ND	ND
pH	5	4	5	7	11	11	11	11
Yield[c]	42	30	38	ND	250	187	259	384

[a] P=pine, S=spruce, B= birch, St=straw.
[b] Methanol and ethanol.
[c] Organic matter dissolved in g COD per kg of dried wood or straw.

1. The anaerobic biodegradability of wood and straw pulping wastewaters

The average acidification of the wastewater COD (conversion to methane and VFA) observed during the batch anaerobic digestion of the TMP and the soda pulping wastewaters prepared from wood and wheat straw are reported in Table 3. The acidification of the TMP wastewaters ranged from 68% to 87% of total COD, indicating their high anaerobic biodegradability. In contrast, wastewater prepared in alkaline conditions were poorly biodegradable(approximately 50% acidification), indicating the presence of recalcitrant organic matter in the soda pulp liquors.

2. The methanogenic toxicity of wood and straw pulping wastewaters

The concentration of the various TMP and soda pulping wastewaters resulting in a 50% and 80% inhibition of the methanogenic activity are listed in Table 4. The effect of soda pulping liquors on the methanogeinc activity is also shown in Fig. 1.

As shown in Table 4, TMP wastewaters exerted low toxicity on methane bacteria and did not cause any significant inhibition at concentrations expected in the effluents of paper mills utilizing TMP processes. The 50% IC values obtained in the first feeding ranged 11.5 to 13.7 g COD/*l*, whereas those observed in the second assay feeding were significantly higher, indicating partial recovery of the methanogenic activity. In contrast, soda pulp liquors were highly inhibitory to the activity of methanogenic bacteria, indicating that the contact of wood with alkali con-

Table 4. The concentration(mgCOD/*l*) of the various TMP and soda pulping wastewaters evaluated in this study resulting in a 50% and 80% inhibition of the methanogenic activity.

Pulp	Lignocullulosic material	1st feeding		2nd feeding	
		50% IC	80% IC	50% IC	80% IC
TMP	Pine	11.5	14.0	12.5	14.4
	Spruce	13.0	22.0	22.0	>22.0
	Birch	13.7	17.0	17.4	22.0
	Straw	NT[a]	NT	NT	NT
Soda	Pine	2.1	2.7	2.0	2.8
	Spruce	5.4	8.3	4.8	7.3
	Birch	5.3	7.3	6.8	8.6
	Straw	4.4	7.3	7.5	9.7

[a]NT=non toxic at 3 g COD/*l*, the highest concentration tested.

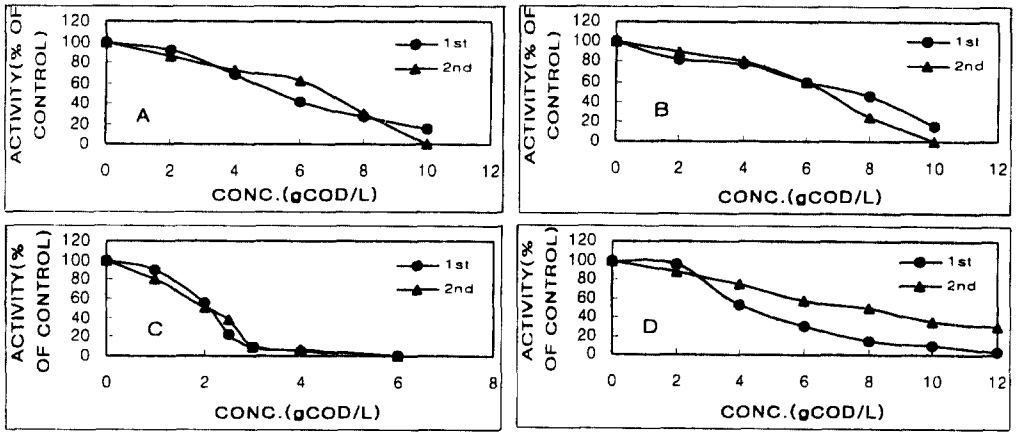

Fig. 1. The methanogenic activity(as percentage of the control activity) of granular sludge exposed to soda liquors prepared from wood and straw(birch, A; spruce, B; pine, C; wheat straw, D).

tributes significantly to increase the methanogenic toxicity of the pulping wastewaters. The COD concentrations resulting in 50% inhibition in the first assay feeding ranged from 2.1 to 5.4 gCOD/*l*, respectively. Alkaline pine wood liquors, with 50% IC corresponding to 2.1 g COD/*l*, were distinctly more inhibitory than soda pulp liquors prepared from other lignocellulosic feedstocks. The residual methanogenic activities determined in the second feeding that followed the 2 week exposure to the pine and spruce soda pulping liquors were slightly lower as compared to those obtained in the first feeding. The persistence of the inhibition beyond exposure indicates a damaging effect of the toxicants on the sludge. Partial recoveries of the methanogeinc activity were evident in the toxicity assays with alkaline liquors prepared from birch wood and straw since somewhat higher inhibitory concentrations were observed in the second compared to the first feeding.

Batch digestion experiments with repeated feedings of straw and spruce soda pulp water were also performaned to evaluate the short-term adaptation capacity of the sludge to these wastewater. The procedure for the additional feedings was similar to that applied to assay the methanogenic toxicity of the soda pulp liquors in the first feeding. The 50% and 80% IC resulting from exposure of granular sludge to five consecutive feedings of straw alkaline liquor are given in Fig. 2.

According to these results, a significant increase in the inhibiting concentration with feeding number was observed, indicating that granular sludge can adapt to a great extent to the inhibitory effects of straw sods pulp liquor. In contrast, repeated feedings with spruce soda pulping wastewater did not result in any adaptation of the granular sludge, and the 50% and 80% IC values determined in the first and third assay feeding were very similar.

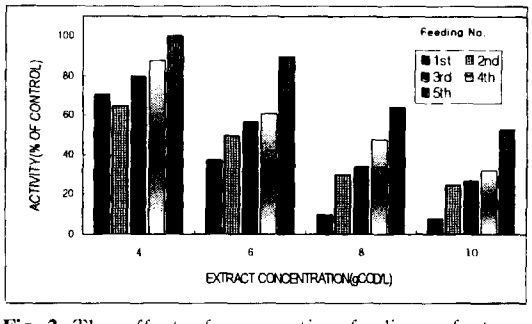

Fig. 2. The effect of consecutive feedings of straw soda pulping liquor on the activity of methanogenic granular sludge.

3. Source of methanogenic inhibition in soda pulping wastewater

Additional experiments were conducted in an attempt to identify the sources of the inhibition in soda pulping liquors. The detoxification obtained by selectively removing specific wastewater components was evaluated in anaeorobic toxicity assays fed the original and treated wastewaters. The treatments applied included liquid-liquid extraction with ether, XAD and PVP adsorption, calcium and acid precipitation. The extraction of wood derived wastewaters with ether removes hydrophobic resin components, such as fatty acids, resin acids, esters, waxes and sterols.[15] Adsorption onto XAD-2 under alkaline(pH 9) conditions has previously been used to isolate wood resin compounds from pulp and paper effluent samples. PVP is a polyamide that specifically removes the fraction of the wastewater with tannic qualities. The calcium can precipitate an important fraction of the dissolved lignin, but its effectiveness is restricted to the intermediate to high molecular lignin derivatives. Fatty and resin acids are also removed by calcium precipitation. Acidification precipitates lignin and resin compounds similarly as calcium.

The elimination of COD in the treatment with PVP, XAD, calcium and ether was low, ranging between 13 and 20% of the total wastewater COD. In contrast, precipitation in acidic medium resulted in removal of 67% of the total wastewater COD. The influence of various treatments of pine alkaline pulp liquor on the methanogenic activity of granular sludge exposed to the resulting wastewaters is illustrated in Fig. 3.

Extraction with ether, method specific for wood resin components, almost completely removed wastewater toxicity. Other method which remove resin compounds such as XAD-2 adsorp-

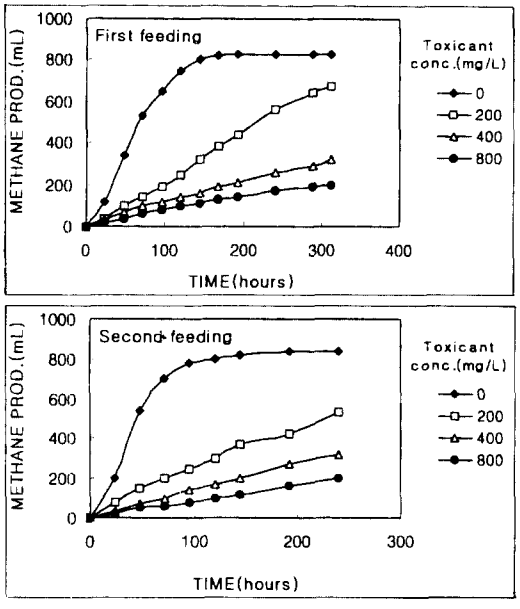

Fig. 3. The influence of various treatments of the pine soda pulping liquor on the methanogenic activity of granular sludge exposed to the different extracts in the first and in the second assay feeding.

tion, acid and calcium precipitation were also able to completely detoxify the wastewater. PVP adsorption, on the other hand, had only a small effect on removing the toxicity, indicating that organics with tannic qualities did not significantly contributes to the high toxicity of the soda pulp waters. Finally, the inhibitory effect of the insoluble fraction upon acid precipitation was close to that exerted by the untreated wastewater. Although not illustrated, these treatment gave similar results with spruce soda pulp liquors. These results indicate that the inhibitory components in coniferous wood extracts were insoluble at acidic pH and could be precipitated by calcium. Furthermore, the non-toxicity of the ether extracted liquors strongly suggests that the major inhibitory compounds are the wood resin constituents.

Finally, it should be noted that the composition of the apolar extractive of straw significantly differs from that of wood. The methanogenic toxicity of straw apolar extractives was not assessed and therefore, it is not certain whether the inhibitory potential of straw soda pulp liquor is caused by resinous of other lignocellulosic derivatives released during alkaline pulping.

4. The methanogenic toxicity of soda pulp liquors from resin-free coniferous wood.

To further investigate the inhibitory role of resin compounds, pine wood was extracted with organic solvents to remove resin prior to alkaline pulping. The effect of alkaline liquors prepared from both untreated pine wood and treated resin-free pine wood on the methanogenic activity was tested. As shown in Fig. 4, removing the wood resin resulted in an almost complete detoxification of the soda pulp water. It should be noted that non-resinous components may also contribute somewhat, though to a much lesser extent, to the inhibitory activity of alkaline liquors as indicated by the low inhibition caused by the resin-free pulp liquor, as listed in Table 5.

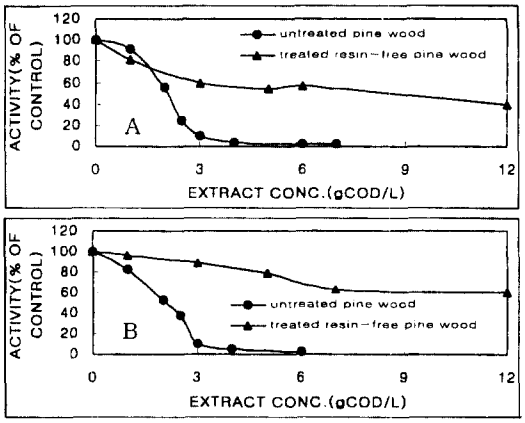

Fig. 4. The effect of soda pulping wastewaters from untreated pine wood and treated resin-free pine wood on the methanogenic activity of granular sludge(A. first assay feeding; B, second assay feeding).

Table 5. The concentration(mgCOD/*l*) of soda pulping liquors from pine wood and resin-free pine wood resulting in a 50% and 80% methanogenic inhibition

Pine wood	1st feeding		2nd feeding	
	50% IC	80% IC	50% IC	80% IC
Untreated	2.1	2.7	2.0	2.8
Resin-free	9.0	20.0	>12.0	>12.0

IV. Discussions and Conclusions

In this study we have demonstrated that the anaerobic treatability of pulping wastewaters is largely dependent on the pulping method applied to a smaller extent on the type of lignocellulosic feedstocks used as raw material. Wastewaters derived from soda pulping were less biodegradable and they caused significantly higher methanogenic inhibition as compared to those derived from TMP. The significant differences observed in the anaerobic biodegradability and methanogenic toxicity of TMP compared to soda pulping effluents can be explained by the distinct effect of each pulping method in controlling the type and quantity of lignocellulosic components solubilized into the wastewater.

During mechanical pulping processes, carbohydrate are the principal components extracted. The wood is subjected to high pressure and temperatures under slightly acidic conditions in which hemicellulose is largely dissolved and lignin is attacked only to a minor extent. In the resulting effluents carbohydrates may account for 50% to 70% and lignin or 15% to 30% of the total wastewater dry solids.[4] The wood resin constituents are poorly soluble in acidic conditions and therefore only low concentrations are expected in mechanical pulping effluents. On the other hand, pulping in alkaline conditions solubilizes to a large extent both the hemicellulosic and lignic fractions. The lignin content of the alkaline pulping liquors can account for up to 50% of the total solids. The high lignin content is responsible for the characteristic strong brown color of these wastewaters. Alkaline pulping process also effectively extract wood resin constituents, resulting in the presence of important quantities of resin derived components in the process relief gases and in the black liquor.

The anaerobic biodegradability of TMP effluents was high due to the large fraction of readily biodegradable carbohydrates in these wastewaters. The distinctly lower biodegradability of alkaline pulping liquors can be explained by their higher lignin content. Past research indicates that anaerobic bacteria have a very limited capacity to degrade lignin.[16] The recalcitrance of lignin in anaerobic environment is related its characteristic chemical heterogenity and high molecular weight. In any case, the anaerobic metabolism of various lignin monomers and oligomers(molecular weight <800 dalton) has been reported.[17]

Numerous types of forest industry wastewaters contain important amounts of lignin. Chemical processes such as bleaching and kraft, soda and sulfite pulping effectively extract lignin into the wastewater. The limited capacity of anaerobic microorganisms to degrade lignin indicates that other technologies, including physical-chemical and enzymatic or fungal treatment should be applied to remove the color bearing lignic COD which is resistant to anaerobic as well as conventional aerobic wastewater treatment. The toxicity of pulping wastewaters was found to depend strongly on the pulping conditions used. Wastewater derived from the TMP process were only mildly toxic to methane bacteria. In contrast, the wastewaters of soda pulping caused severe methanogenic inhibition at low concentrations as shown in Table 4. The toxicity of soda pulp wastewaters also depended on the type of lignocellulosic feedstock used. Pine wood was responsible for the soda pulp liquor with highest toxicity. Birch wood and straw alkaline pulp liquors were the least inhibitory.

Selective removal of various fractions from the soda extract with different physical-chemical treatments indicated that wood resin constituents were responsible for most of the toxicity associated with the alkaline liquors of wood. The methanogenic toxicity of wood resin was confirmed by comparing the inhibitory effect of soda pulp waters prepared from pine wood and resin-free pine wood. These observations are supported by previous literature reports indicating the high methanogenic toxicity of individual resin constituents such as volatile terpenes, resin acids and long chaining olatile fatty acid.[18] Moreover, resin compounds are also implicated in the aquatic toxicity of forest industry effluents. Although wood resin was responsible for most of the methanogenic toxicity, the soda pulp liquor derived from resin-free pine wood exerted a

small inhibitory effect, indicating that non-resinous compounds may also components most likely correspond to lignin derived phenolics. Low molecular weight lignin derivatives have previously been identified as microbial inhibitors in aqueous lignocellulosic extracts and in studies with model compounds.

The high methanogenic toxicity of soda pulp liquors as compared to those of TMP demonstrate that the contact of wood with alkali has an important effect in increasing the methanogenic toxicity of wood derivatived wastewaters. The forest industry applies various bleaching and chemical pulping processes where wood is subjected to alkaline treatment. This will generate effluents with high concentrations of resin compounds that are responsible for severe methanogenic toxicity.

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