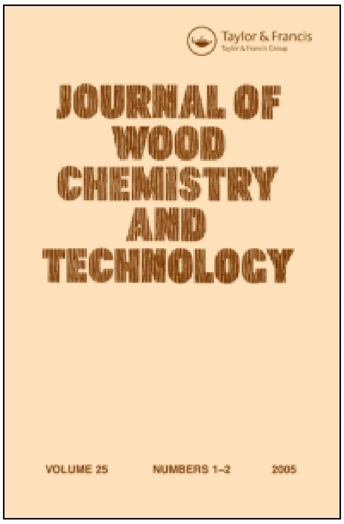

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Cellulose Derivatives Derived From Pulp and Paper Mill Sludge

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CELLULOSE DERIVATIVES DERIVED FROM PULP AND PAPER MILL SLUDGE

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ABSTRACT

Cellulose derivatives were produced from the cellulose fraction of pulp and paper mill sludge. The raw primary sludge was reacted under conventional cellulose derivatization conditions and the modified cellulose was isolated, in most cases, by dissolution in a suitable solvent. The cellulose derivatives produced were cellulose nitrate, cellulose acetate, carboxymethylcellulose, hydroxyethylcellulose, and methylcellulose. These compounds were characterized by Fourier transform infrared spectroscopy and carbon 13 nuclear magnetic resonance spectroscopy.

INTRODUCTION

An ongoing concern of the pulp and paper industry is the disposal of solid wastes (sludge) generated during the mechanical and chemical processing of wood and pulp. Stringent environmental regulations, the expense incurred in transporting sludge, and the rising cost of land for sludge disposal has sparked interest in alternative uses and disposal practices. One unexplored application of sludge is the conversion of the cellulose fraction into cellulose derivatives. Thus, simultaneously creating a valuable commercial product and reducing the quantity of solid waste.

Primary sludge refers to the concentrated material which is obtained by clarifying the waste effluent with techniques such as

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sedimentation, flotation, and filtration. It may contain fiber, bark particles, shives, grit, and fillers such as clay[1]. A particle size distribution study of primary sludge demonstrated that one third of the material remained on screens of mesh size 72, 100, or 150, and was considered fiber[2]. McGovern and coworkers characterized the combined primary and secondary sludge from seven treatment facilities and found that the total carbohydrate content ranged from 23.5 to 36.2%, and the ash content was 27.7 to 38.1% [3].

The work discussed here focuses on the carbohydrate, specifically the cellulosic, portion of primary sludge. The raw sludge is treated with specific chemicals to produce a cellulose derivative. Then the modified cellulose is isolated from the remainder of the sludge by dissolving it in an appropriate solvent. Carboxymethylcellulose, hydroxyethylcellulose, methylcellulose, cellulose nitrate, and cellulose acetate are produced in this manner.

The commercial applications of cellulose derivatives are various and numerous. For example, the acetate and nitrate esters of cellulose are used in plastics, lacquers, and films. Cellulose nitrate has also been employed in explosives and propellants, while cellulose acetate is used in fabrics[4]. The applications of carboxymethylcellulose include its use as a thickening agent for dyestuffs, in foods and pharmaceuticals to control rheology and water content, in drilling fluids, adhesives, cosmetics, and paper sizing[5]. Methylcellulose and hydroxyethylcellulose have also been used as components in cosmetics and adhesives. Hydroxyethylcellulose has additional uses in emulsion polymerization and as a thickener in latex paints[5].

RESULTS AND DISCUSSION

A large U.S. pulp and paper company provided three primary sludge samples. Two of the samples were from the landfill site of a southern U.S. mill and are referred to as L1 and L2. This mill produces groundwood pulp, bleached kraft pulp, and newsprint from predominantly a southern pine feedstock. The third sample was obtained from the primary clarifier of a northern U.S. tissue mill and is labelled C1. The tissue mill uses purchased pulp, of which 25% is recycled fiber, and is composed of approximately 60% softwoods and 40% hardwoods. The sludge samples were characterized in terms of ash, acid insolubles, and the degree of polymerization (DP) of the cellulose fraction. The cellulose derivatives were produced mainly from sludge L2.

Sludge Characterization

Ash is a term generally used to refer to inorganic substances such as silicates, sulfates, carbonates, or metal ions[6]. The ash content of the sludges is presented in column one of Table 1. The high ash level, 51.60%, for L2 is probably due to a high concentration of calcium carbonate. The FTIR (Fourier transform infrared) spectrum of L2 (Figure 1) contains two sharp peaks at 880 and 720 cm^{-1} and a broad band at 1430 cm^{-1}. This absorption pattern is quite similar to that of calcium carbonate[7].

The Klason lignin procedure was used to obtain a rough estimate of the lignin concentration in the sludge samples. This method of analysis was designed for wood and pulp and is not entirely appropriate for sludge. For example, the silicates present in sludge are acid insoluble and, hence, are included as lignin in the results. To correct this, the acid insoluble material is ashed and appropriate adjustments made to obtain a corrected acid insolubles value (Table 1).

The carbohydrate portion of the sludge samples was characterized as the percentage of glucose, xylose, galactose, arabinose, and mannose (Table 2). From the glucose concentration it is possible to estimate the cellulose content if a correction factor is used to subtract the amount of glucose present as galactoglucomannan or glucuronoxylan. As stated previously, the mill from which sludge L2 was obtained uses a southern pine feedstock. Thus,

TABLE 1

Ash Content and Acid Insoluble Material Present in Sludge

Sludge	Ash (%)	Total Acid Insolubles(%)	% Ash in Acid Insolubles	Corrected[a] Acid Insolubles(%)
L1	39.92	31.98	11.61	28.28
L2	51.60	15.30	8.26	14.04
C1	27.86	32.78	76.42	7.73

[a] Total acid insolubles less the contribution of inorganic (ash) material

TABLE 2

Carbohydrate Content of the Sludges[a]

Sludge	%GLU	%XYL	%GAL	%ARA	%MAN	%CELL[b]
L1	19.01	3.33	1.50	0.54	5.40	17.5
L2	20.4	3.6	1.7	1.6	5.2	18.9
C1	31.15	5.11	0	0.07	3.12	30.4

[a] GLU=glucose; XYL=xylose; GAL=galactose; ARA=arabinose; MAN=mannose; CELL=cellulose

[b] estimation based on glucose content

the major hemicellulose component is galactoglucomannan. Assuming a glucose to mannose ratio of 1:3.5 in galactoglucomannan, the estimated cellulose content of sludge L2 is 18.9%.

The molecular weight distribution of the cellulose fraction of sludge C1 and L2 was determined by high pressure liquid chromatography (HPLC) using the technique of Schroeder and Haigh[8]. A

TABLE 3

Molecular Weight and DP of Cellulose in Sludge

Sludge	Molecular Weight (number average)	Molecular Weight (weight average)	DP (weight average)
L2	232013	1100440	2118
C1	134799	562444	1083

cellulose tricarbanilate is generated, dissolved in tetrahydrofuran, and analyzed by HPLC. The molecular weight data for cellulose in sludge C1 and L2 are summarized in Table 3.

Cellulose Derivatives Produced from Sludge

Carboxymethylcellulose (CMC) was produced from both oven-dry and wet (59% water) sludge L2. The sludge was dispersed in isopropanol and an alkali cellulose was generated with sodium hydroxide; this intermediate was then converted to CMC with monochloroacetic acid. Since water is a known solvent for CMC with a DS (degree of substitution) in the range of 0.5-1.2 [9], the reacted sludge was dispersed in water. The soluble CMC was then isolated from the remainder of the sludge by centrifugation. The FTIR spectra of CMC produced from wet sludge L2, CMC from α-cellulose, α-cellulose, and sludge L2 are shown in Figure 1. The salt form of the carboxyl associated with the carboxymethyl pendant group absorbs at 1600 cm^{-1}. The CMC derived from sludge also contains a band at 1730 cm^{-1}, which is due to the free acid form of the carboxyl. This 1730 cm^{-1} band is reduced if the CMC is isolated from the sludge with a dilute aqueous sodium hydroxide solution. The ester of the carboxymethyl group absorbs at 1220 to 1100 cm^{-1}; the same region as the C-O-C bridge, -O-H, and -C-O absorptions associated with the cellulose backbone[10].

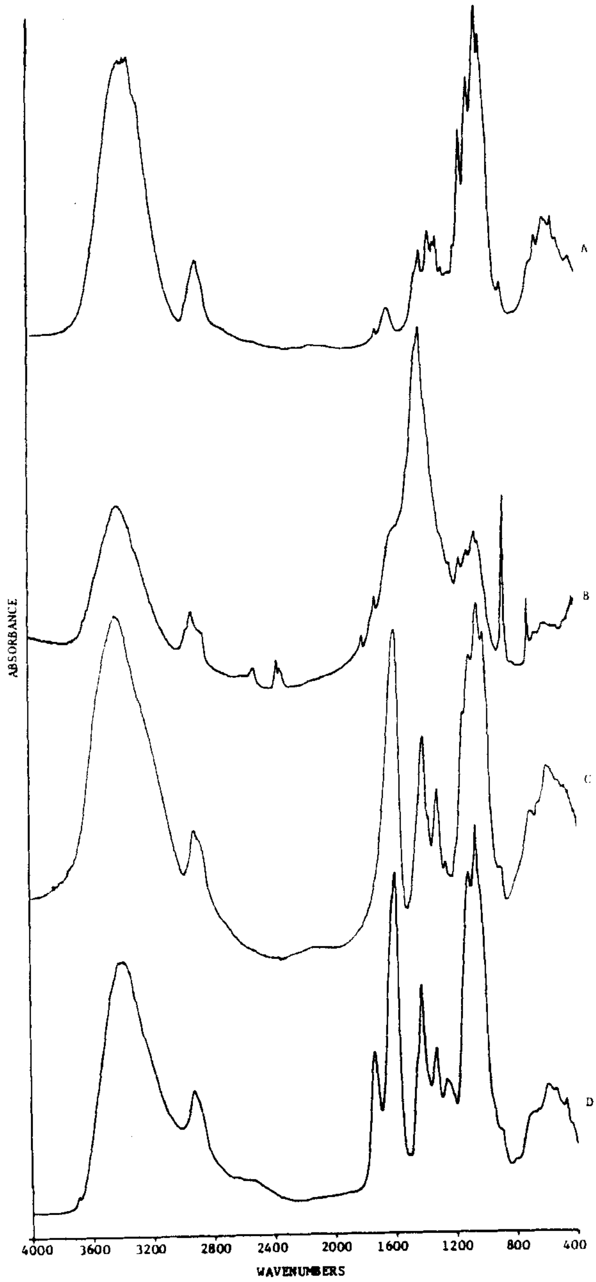

FIGURE 1. FTIR spectra of (A) α-cellulose, (B) sludge L2, (C) CMC produced from α-cellulose, and (D) CMC produced from sludge L2.

Hydroxyethylcellulose (HEC) produced from wet sludge L2 was isolated by dissolution in a dilute aqueous sodium hydroxide solution. From the FTIR of this compound (Figure 2), it is apparent that the oxyethyl (or hydroxyethyl) substituents absorb in the same general regions as cellulose. A minor difference is noted in the CH stretching bands located at 3000 to 2760 cm^{-1}. While cellulose exhibits one peak centered at 2900 cm^{-1}, the HEC derivative shows two peaks at 2920 and 2880 cm^{-1}. A similar absorption pattern has been noted for ethylcellulose, with bands at 2959 and 2857 cm^{-1} [11].

To substantiate the formation of HEC from sludge L2, the product was analyzed by carbon 13 nuclear magnetic resonance spectroscopy (^{13}C nmr). The spectrum for sludge derived HEC (Figure 3) is nearly identical, except for resolution differences, to that obtained by DeMember *et al.* [12] for pure HEC. Also shown in Figure 3 is a single HEC residue showing the carbon numbering system. By comparison with DeMember's study it is possible to assign the intense peaks at 69.16, 71.33, and 60.08 ppm to carbon atoms C7, C8, and C9, respectively, of the oxyethyl substituent. The broader band at 101.9 ppm is assigned to C1, while the peak at 60.46 ppm is due to the unsubstituted C6 of the anhydroglucose ring. When the primary hydroxyl contains a substituted oxyethyl group, the C6 peak is shifted downfield to 69.48 ppm. The three broad bands centered at 81.07, 77.99, and 73.40 ppm in Figure 3 are caused by a combination of the substituted and unsubstituted carbons C2 and C3, as well as C4 and C5 [12]. From the ^{13}C nmr, it is apparent that the product isolated from the reacted sludge L2 is HEC.

Methylcellulose was produced from sludge L2 using either (1) a dimethyl sulfoxide/paraformaldehyde (DMSO/PF) cellulose solvent system and methylating with methyl iodide in the presence of sodium hydroxide, or (2) first exposing the sludge to sodium hydroxide and methylating with dimethyl sulfate. Through infrared techniques it was possible to verify the formation and isolation of methylcellulose via method 1. Zhbankov cites IR stretching

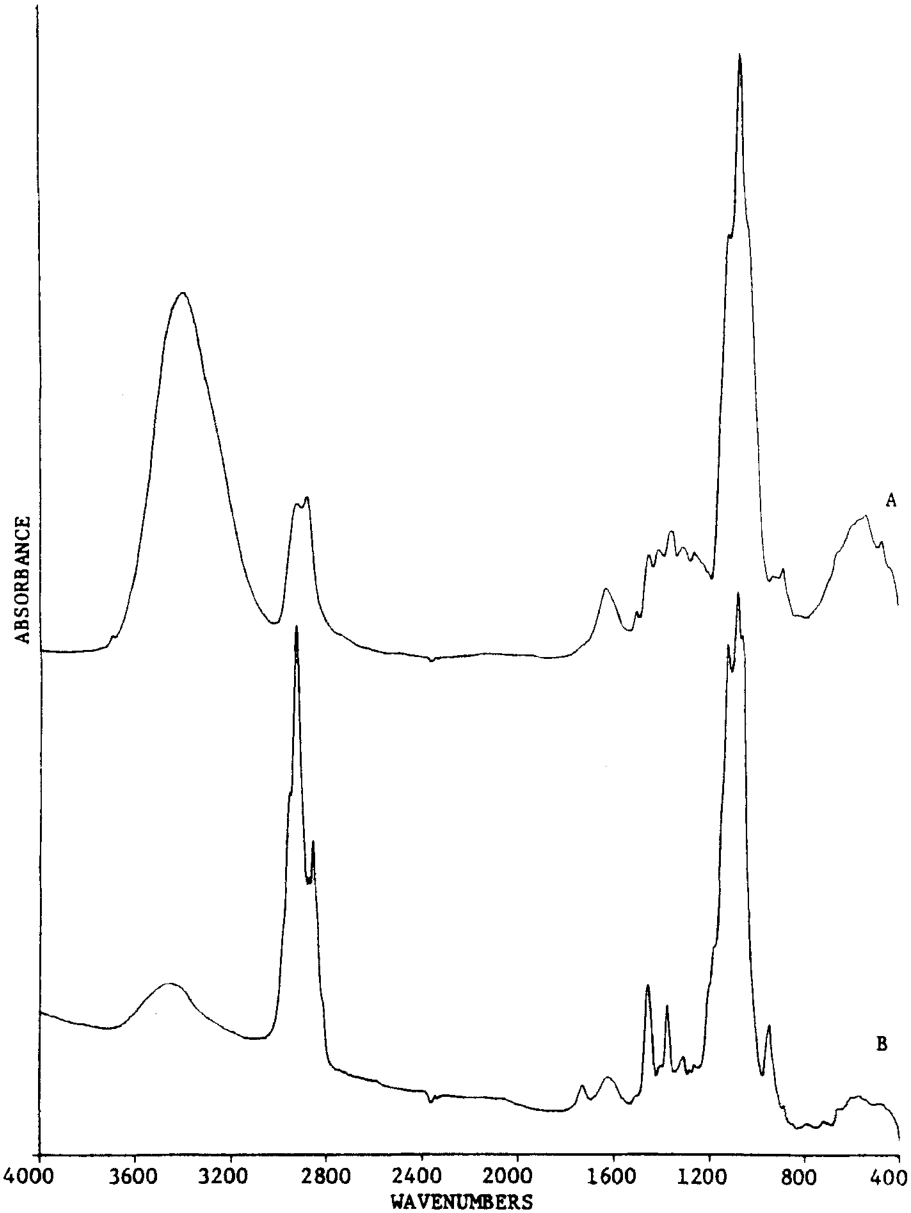

FIGURE 2. FTIR spectra of hydroxyethylcellulose (A) and methylcellulose (B) produced from sludge L2.

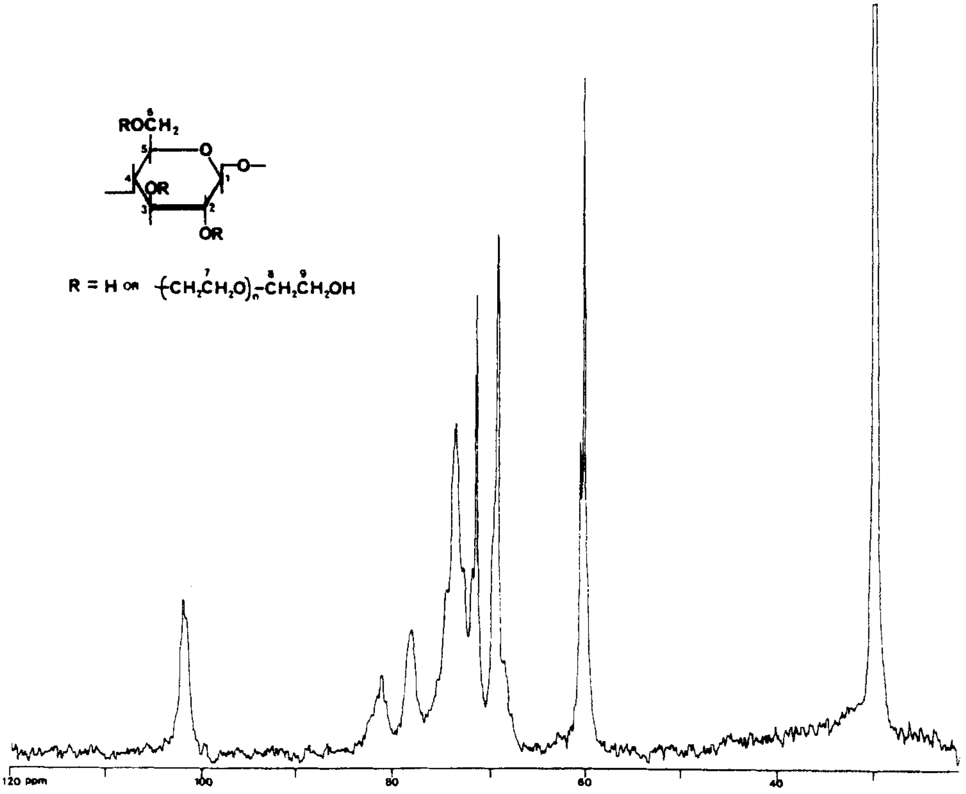

FIGURE 3. ^{13}C nmr spectrum of hydroxyethylcellulose produced from sludge L2.

vibrations at 2970, 2920, 2870, 2830, and 2810 cm^{-1} for methylcellulose^{10}. The product from method 1 shows intense peaks at 2920 and 2850 cm^{-1}, with smaller peaks at 2950 and 2870 cm^{-1} and a shoulder around 2810 cm^{-1} (Figure 2). The intensity of the bands in this region of CH stretching is much greater than in the case of α-cellulose. Also noted in Figure 2 is the decrease in the absorption associated with the hydroxyl group of cellulose, which reflects the extent of methylation. The methyl deformation vibrations appear at 1460, 1370, 1310, and 950 cm^{-1}.

The methylcellulose produced by method 2 was isolated from the sludge by dissolving in water. This method appears to produce less methylation of the cellulose. The FTIR of the product has a CH stretching region that is far less intense than that of the methylcellulose produced by method 1. A very small peak appears at 940 cm^{-1}, presumably associated with methyl deformation.

Cellulose nitrate was prepared by exposure of oven-dry sludge L2 to a nitrating solution and separated from the remainder of the sludge by its characteristic acetone solubility. The nitrate group is easily identified by FTIR spectroscopy (Figure 4). The intense peaks at 1650 and 1270 cm^{-1} are due to the stretching vibrations of the nitro group, and the absorption at 830 cm^{-1} is associated with the nitrate ester[13]. It is also apparent that the nitrate substitution greatly decreases the hydroxyl stretching peak at 3600-3200 cm^{-1}.

Further evidence that the product isolated from nitrated sludge L2 is indeed cellulose nitrate was obtained by analysis of the ^{13}C nmr spectrum (Figure 5). Wu has published several ^{13}C nmr spectra of cellulose nitrate with various degrees of substitution (DS)[14]. The spectrum of sludge derived cellulose nitrate is very similar to that published for cellulose nitrate with a DS of 3. The components of the ^{13}C nmr spectum of cellulose nitrate from sludge L2, as well as the peaks associated with cellulose trinitrate reported by Wu[14] and Clark *et al.*[15] are summarized in Table 4. The correlation of the ^{13}C nmr peaks with the carbon atoms of the nitrated β-D-glucopyranose residue follow the convention of Clark *et al.*[15] In Table 4, the peak values reported by Clark *et al.* are about 1.5 ppm downfield of the values obtained for cellulose nitrate from sludge and those published by Wu for cellulose trinitrate. This may reflect the difference in internal references. The band due to DMSO at 39.5 ppm was used as the reference in Figure 5, while Clark et al. used tetramethylsilane. A small peak is visible at 96.88 ppm in the ^{13}C nmr of cellulose nitrate from sludge. Clark *et al.* assigned this peak to the C1 in a 2,6-dinitrated residue. However, other bands associated with partially nitrated material are not visible in Figure 5.

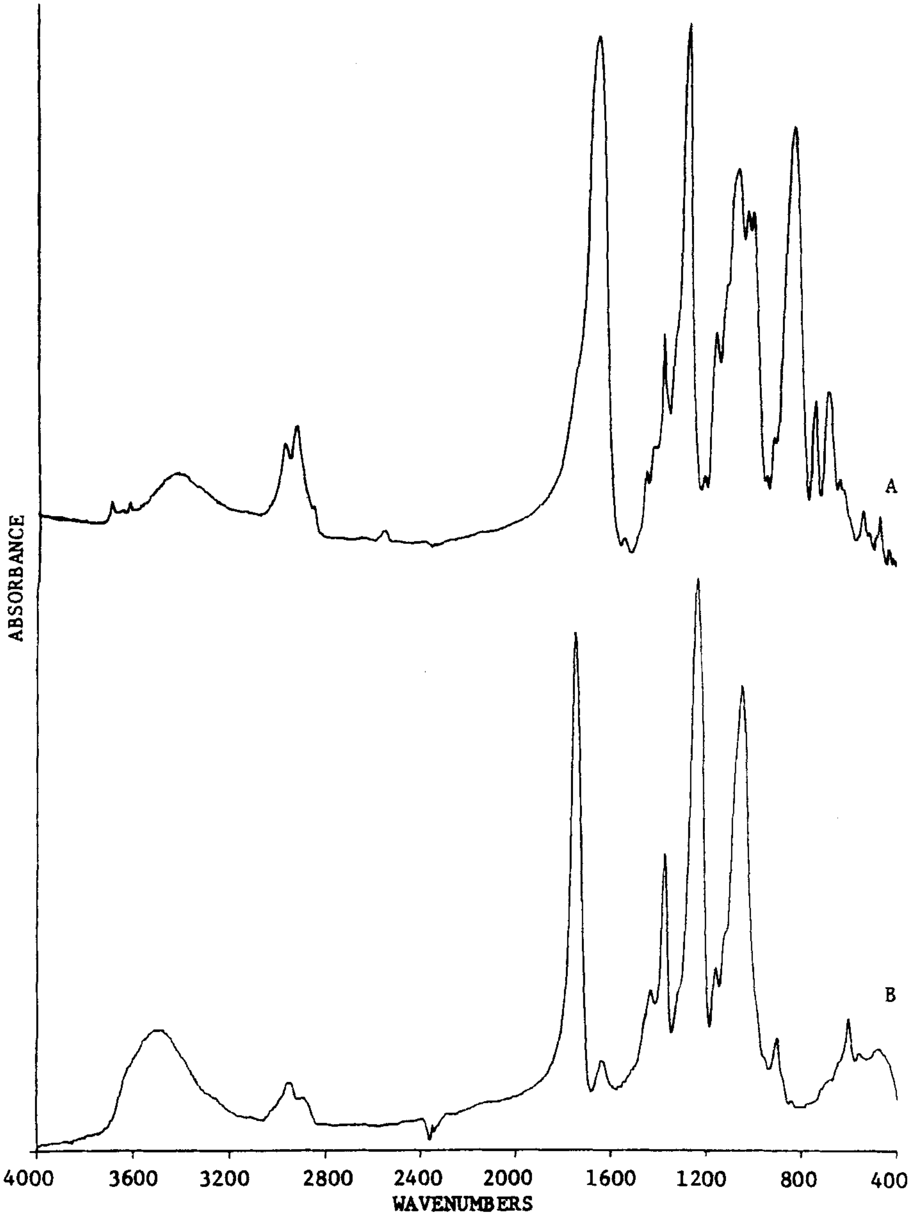

FIGURE 4. FTIR spectra of cellulose nitrate (A) and cellulose acetate (B) produced from sludge L2.

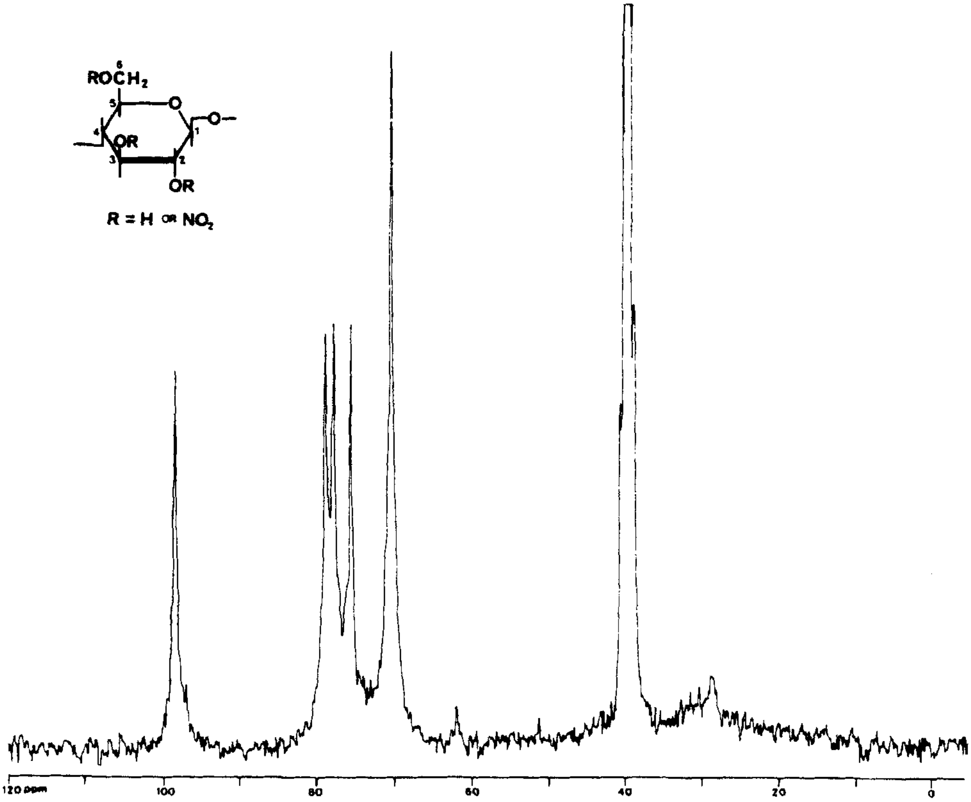

FIGURE 5. ^{13}C nmr spectrum of celluose nitrate produced from sludge L2.

Cellulose acetate was isolated from an acetylation reaction conducted on sludge L2 by dissolving it in a mixture of dichloromethane and methanol (9:1 by volume). The FTIR spectrum of this cellulose acetate is shown in Figure 4. The absorptions associated with the acetyl substituent occur at 1750 cm^{-1}, due to the carbonyl; 1430 and 1370 cm^{-1}, due to methyl deformation; and 1240 and 1050 cm^{-1}, due to ester stretching[10].

TABLE 4

Peak Assignments for ^{13}C nmr Spectra of Cellulose Nitrate Samples[a]

Carbon Atom	Cellulose Nitrate from Sludge L2	Cellulose Trinitrate (Wu[14])	Cellulose Trinitrate (Clark *et al.*[15])
C1	98.19	98.2	99.7
C2	75.41	75.5	76.9
C3	78.66	78.7	80.2
C4	77.57	77.6	79.1
C5,C6	70.08	70.1	71.6

[a] Values are in ppm

TABLE 5

Percent Yield of Cellulose Derivatives Produced from Sludge L2

CN	CA	CMC	HEC	MC1	MC2[a]
72.9	72.3	86.3	64.3	88.8	25.6

[a] CN=cellulose nitrate; CA=cellulose acetate; CMC=carboxymethylcellulose; HEC=hydroxyethylcellulose; MC1=methylcellulose (DMSO/PF method); MC2=methylcellulose (dimethyl sulfate method)

Yield Values for Sludge Derived Derivatives

The estimated percent yield for the various cellulose derivatives formed from sludge are summarized in Table 5. The calculations are based upon a cellulose content of 18.9% in the sludge L2. The DS, and molar substitution in the case of HEC, are approximated from the solubility properties and the values quoted for the various procedures. According to the yield values, methylcellulose produced by the dimethyl sulfate method (method 2) is much less successful than the DMSO/PF procedure (method 1). The latter method is a homogeneous reaction where the crystallinity of the cellulose is disrupted; hence, the cellulose hydroxyls are presumably more accessible to the methylating agent.

CONCLUSIONS

An alternative to direct land disposal of primary sludge is to use the sludge as a raw material for production of cellulose derivatives. The sludge can be reacted under standard derivatizing conditions and the modified cellulose recovered by dissolution in a suitable solvent. Using this technique, carboxymethylcellulose, hydroxyethylcellulose, methylcellulose, cellulose nitrate, and cellulose acetate were produced from sludge (L2) with yield values ranging from 64.3 to 88.8% (based on the estimated cellulose content of sludge L2).

The cellulose derivatives produced from sludge contain small amounts of impurities, as is evident from the tan color of the product. Small amounts of lignin are probably responsible for the coloration. The product may also contain some derivatized hemicelluloses. However, the relative amount of these substances is believed to be minimal.

The cellulose derivatives formed from sludge have numerous potential commercial applications. Sludge derived cellulose nitrate and acetate can be used as protective lacquers or plastics where the product is colored or dyed. The sludge derived cellulose ethers can be used as components of adhesive formulations. In addition, large volumes of sludge derived CMC could be used in drilling fluids and as paper sizing for corrugating board. HEC could also be used as a thickener in colored latex paints.

EXPERIMENTAL

Sludge Characterization

The amount of ash present in the sludge samples was determined using Tappi standard T15m-58. The acid insoluble material was measured by Tappi standard T222m-54. HPLC techniques were used to determine the concentration of glucose, galactose, mannose, xylose, and arabinose. The instrumentation consisted of a Waters HPLC operated at 48°C and a Bio-Rad HPX87P column.

The molecular weight and DP of the cellulose fraction of the sludge was also measured by HPLC methods using the technique of Schroeder and Haigh[8]. The lignin was first removed from the sludge by the acid chlorite method for generating holocellulose from wood[16]. The remaining carbohydrate material was reacted with phenyl isocyanate in pyridine to generate cellulose tricarbanilate (CTC). The excess phenyl isocyanate was destroyed with a small quantity of methanol. The soluble CTC was isolated by centrifugation and subsequent precipitation in methanol. The CTC, which was dried over phosphorous pentoxide, was dissolved in tetrahydrofuran (THF) and injected into the HPLC. The HPLC unit consisted of a Perkin-Elmer Sigma Series 2 pump, Sigma Series 15 data station, LC-85 UV detector set at 235 nm, and Shodex columns A/804 and A/805. The liquid phase was THF and polystyrene standards were used for calibration.

Cellulose Derivatives Produced from Sludge

CMC was produced from wet sludge L2 by adapting the procedure described by Browning for pulp[16]. Wet sludge (19.7 g), with a moisture content of about 59%, was suspended in 400 ml of isopropyl alcohol. Over a period of 30 min., 10 g of NaOH dissolved in 7 ml of water was added to the suspension. Monochloroacetic acid (9 g) was added over 30 min. with stirring. The reaction flask was then placed in an oven at 55°C for 3.5 hr. with occasional stirring. The solid material was filtered, dispersed in methanol, and neutralized with 90% acetic acid. The solids were washed several times with 75% ethanol and finally with absolute methanol. The CMC was recovered by dissolving in water, centrifuging to remove the insoluble material, and freeze drying.

HEC was produced from wet sludge L2 by first generating an alkali cellulose and then reacting it with ethylene oxide[17]. A mixture of 25 g wet sludge L2, 200 ml isopropyl alcohol, and 4 g NaOH dissolved in 20 ml of water was stirred for 1 hr. to swell the cellulose. Ethylene oxide was bubbled through 50 ml of isopropanol until approximately 10 g had dissolved. The ethylene oxide and alkali sludge solutions were combined and placed in an oven at 55°C for 5.5 hr. The solid material was collected and neutralized in 75% methanol with acetic acid and washed 4 times with 75% methanol. The HEC was recovered by dissolving it in a dilute aqueous NaOH solution. Material that was insoluble was removed by centrifugation. The HEC solution was dialyzed with deionized water to remove salts and NaOH. The resultant aqueous HEC solution was freeze dried.

Two different methylating procedures were applied to sludge L2. The first method was described by Nicholson and Johnson for methylating cellulose in the dimethyl sulfoxide (DMSO)/paraformaldehyde (PF) solvent system[18]. Oven-dry sludge L2, 1.53 g, was combined with 100ml DMSO and 4.25 g PF (Fluka AG, Chimische Fabrik). This mixture was heated slowly, over 20-30 min., with rapid stirring to 120°C. The temperature was decreased to 80°C and an additional 1 g of PF was added. Again the temperature was increased slowly to 135°C. The final temperature was sufficient to decompose excess PF. At this stage the unwanted components of the sludge were removed by centrifugation, leaving the methylolcellulose in solution with the DMSO. Sodium hydride (2 g, 50% mineral oil) was washed with petroleum ether, added to the DMSO/-methylolcellulose solution, and stirred slowly for 2 hr. Methyl iodide (3 ml) was then added and the reactants stirred for 24 hr.

at room temperature. The sodium hydride and methyl iodide steps were repeated a second time. A solution of formic acid and water (50 ml, each) was added to the reaction mixture. The contents were dialyzed for 3-4 days and freeze dried.

The second method of methylation was adapted from a procedure to methylate mercerized cellulose[19]. Sodium hydroxide (150 ml of a 30% aqueous solution) was added to 7.55 g of wet sludge L2. After 1 hr., the mixture was centrifuged and the alkali solution removed by decantation. The sludge, still wet with 30% NaOH, was allowed to age for about 1 hr. The sludge was dispersed in 150 ml of toluene and dimethyl sulfate (15 ml) was added dropwise. The reaction mixture was stirred under nitrogen for 18 hr. The toluene was removed by filtration and the solids washed with 90% acetic acid (50 ml) in methanol (250 ml), and several additional times with methanol. The product was isolated by dissolving it in water, centrifuging to remove insoluble material, and freeze drying.

Cellulose nitrate was generated from sludge L2 by reaction with a nitration mixture of fuming nitric acid and acetic anhydride[16]. Nitric acid (75 ml of a 90% aqueous soultion) was cooled to -20°C in a dry ice/acetone bath. Acetic anhydride (112 ml), cooled to 0°C, was added slowly to the nitric acid. Sludge L2 (1.5 g), which had been oven-dried and fluffed in a blender, was then added to the acid mixture. The reaction flask was sealed and maintained at less than -20°C until the heat of the reaction had dissipated. The reaction mixture was kept near 0°C for an additional 3 hr. with occasional swirling. Most of the nitrating acid was removed by decantation and the product was dispersed in cold water and filtered. The solids were washed with cold water until the filtrate was neutral. The cellulose nitrate was isolated and stabilized by dissolving it in acetone and reprecipitating with petroleum ether.

The procedure for acetylating the cellulose portion of sludge was adapted from a method used to produce cellulose acetate from cotton linters[20]. Wet sludge L2 (8 g) was immersed in water for 15 min., filtered, and dewatered by 3 washings with glacial acetic acid. The sludge was then added to 90 ml of glacial acetic acid containing about 1 ml of sulfuric acid and shaken for 1 min. Acetic anhydride (25 ml) was added and the mixture was shaken vigorously for 1 min. and allowed to react for 1 hr. A solution of water, 4 ml, and acetic acid, 8 ml, was added to the mixture and stirred for 30 min. The contents of the reaction flask were dispersed in water and filtered. The solids were washed with aqueous sodium bicarbonate, followed by water. The cellulose acetate was isolated by dissolving in dichloromethane/methanol (9:1 by vol.), removing the insoluble material by centrifugation, and reprecipitating the cellulose acetate with petroleum ether.

Instrumental Analysis

The FTIR spectra were obtained with a Nicolet 7199 FTIR using KBr pellets. The ^{13}C nmr spectra were recorded with a Bruker WM-250 FT operating at 62.9 MHz. The samples were run overnight (about 10,000 scans) in tubes of 10 mm diameter. The solvent for cellulose nitrate was d_6DMSO with the 39.5 ppm DMSO peak serving as reference. The sample was run at 70°C. The HEC sample was run in D_2O with a trace of acetone as the reference (29.8 ppm). The temperature during acquisition was 37°C.

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