Enzymatic degradation of polygalacturonic acids released from mechanical pulp during peroxide bleaching

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ABSTRACT: Polygalacturonic acids account for about half of the potential "anionic trash" (as measured by polyelectrolyte titration) in peroxide-bleached mechanical pulp. Pectinase treatment of the bleached-pulp suspension or filtrate degrades the dissolved polygalacturonic acid into monomeric galacturonic acid, effectively eliminating the cationic demand caused by this anionic polyelectrolyte. Pectinase treatment shows promise as a means of preventing potentially detrimental polygalacturonic acids from complexing with the cationic polymers that are widely used in papermaking.

KEYWORDS: Anionic compounds, bibliographies, cationic compounds, mechanical pulps, pectinase, pectins, peroxide bleaching, Picea abies, polyelectrolytes, polygalacturonic acid.

Carbohydrates are released from Norway spruce *(Picea abies)* mechanical pulp during peroxide bleaching *(1, 2)*. These carbohydrates are composed primarily of polygalacturonic acids released from the fibers under the alkaline conditions of peroxide bleaching. In the absence of an effective pulp-washing stage—with segregation of the resulting wash water from the mill's water system—these anionic polyelectrolytes—as well as other dissolved and colloidal substances in the pulp suspension—will travel on to the paper machine, where they can adversely affect papermaking.

The dissolved and colloidal materials that negatively affect papermaking are commonly referred to as "detrimental anionic substances" *(3–5)*. The reported detrimental effects include interference with cationic retention/drainage aids, lower wet strength, longer drainage time, deposit formation, reduced sheet brightness, and reduced paper strength *(3–10)*. Many papermakers use the term "anionic trash" to describe the anionic oligomers and polymers that accumulate in the paper machine white-water system and undermine the efficiency of the papermaking process *(11)*. Both "anionic trash" and "detrimental anionic substances" are used interchangeably to refer to the dissolved and colloidal substances that interfere with the efficiency of cationic papermaking polymers by forming polyelectrolyte complexes *(3–6)*.

Anionic polyelectrolytes can react with cationic polyelectrolytes to form polyelectrolyte complexes and/or complex coacervates *(12, 13)*. The molar mass, charge density, polyelectrolyte structure, pH, and ionic strength all affect the complexation of oppositely charged polyelectrolytes.

Polyelectrolyte titration is useful for measuring the amount of anionic polyelectrolytes in water samples and for determining the charge characteristics of papermaking additives and other polyelectrolytes *(5, 14–19)*. Several studies have been done on the complexation of cationic papermaking polymers with model compounds representing the anionic polyelectrolytes present in papermaking systems *(20–23)*. However, no such studies have considered polygalacturonic acids as potential "anionic trash." Because polygalacturonic acids are anionic polyelectrolytes, it is probable that they also will complex with cationic papermaking additives.

Polygalacturonic acids occur in nature as macromolecular constituents of pectic substances *(24, 25)* and are degraded to oligogalacturonic acids

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and, ultimately, galacturonic acid by treatment with suitable pectinases *(24–26)*. The purpose of this study was to determine whether pectinase treatment could be an effective method for degrading the polygalacturonic acids released from mechanical pulp during peroxide bleaching and whether such treatment could be useful in deactivating these potentially detrimental anionic polyelectrolytes.

Results and discussion

Cationic demand of mono-, oligo-, and poly-galacturonic acid solutions

Polygalacturonic acid is a natural anionic polyelectrolyte comprised mostly of galacturonic acid units. The negative charges in polygalacturonic acid solutions originate from ionization of the carboxylic acid group in the galacturonic acid units that compose the polymer. The extent of ionization depends on factors such as pH, ionic strength, polyelectrolyte concentration, and the type of simple electrolytes present in solution. The extent of ionization at a given pH increases with increasing ionic strength and concentration of polygalacturonic acid *(27)*. Ionization at a given pH also increases with decreasing degree of polymerization (DP) for mono-, oligo-, and polygalacturonic acids *(28)*.

Polygalacturonic acids can be more easily ionized than typical synthetic polycarboxylic acids. For example, it has been shown that at pH 5, 80% ionization of polygalacturonic acid occurs in dilute, low-salt solutions *(29)*, while for synthetic polymethacrylic acid and polyacrylic acid, less than 25% ionization occurs under comparable conditions *(30)*.

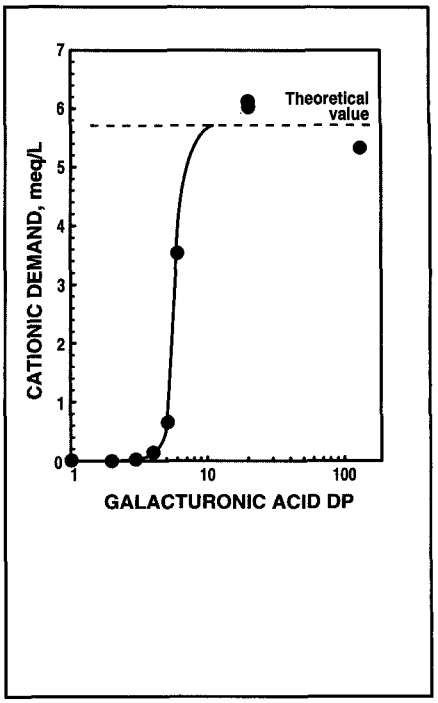
Due to the shielding effect of the polycation in the polyelectrolyte complexes formed, polyelectrolyte titration will typically give a higher degree of ionization, at a given pH, than potentiometric titration *(31)*. Therefore, it is likely that under the conditions used in the polyelectrolyte titrations in the present study (pH 6.5–7), most of the carboxylic acid groups present in the samples would be detectable as ionized groups.

Cationic demand is a measure of the anionic polyelectrolytes, or potential "anionic trash," present in a pulp suspension or water sample and is expressed in units of charge concentration (eq/L) *(32)*. Cationic demand for mono-, oligo-, and poly-galacturonic acid solutions (≈ 1 g/L) was measured by polyelectrolyte titration. **Figure 1** shows that the cationic demand for the various solutions was clearly dependent upon the DP, or molar mass, of the model compounds.

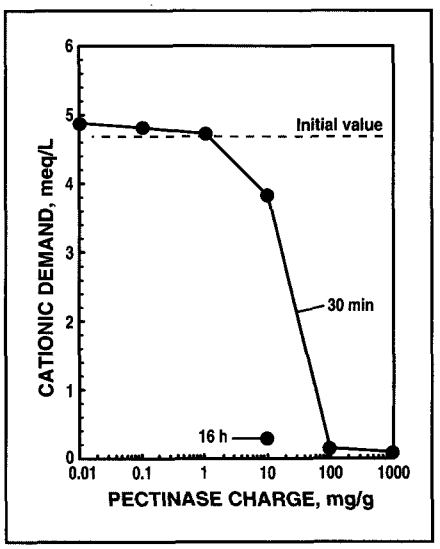
This suggests that there was a minimum polygalacturonic acid DP necessary for complexation to occur between polygalacturonic acid and polybrene (the cationic polymer used to determine cationic demand). Such DP-dependent complexation behavior has been observed in drag-reduction experiments carried out with cationic polyethyleneimine (PEI) of varying DP and synthetic anionic polymers *(33)* and in the competitive interactions of a metachromatic dye and cationic PEI (of varying DP) with potassium polyvinylsulfate (commonly used as the anionic polymer in polyelectrolyte titrations) *(31)*. In the latter study, it was concluded that a minimum number of cationic charges per molecule was needed to bring about cooperative formation of interpolymer complexes. Furthermore, it was shown that for DP values exceeding this minimum criterion, the complexation stoichiometry between oppositely charged polyelectrolytes would be essentially independent of molar mass *(31)*.

Because the concentrations of the mono-, oligo-, and poly-galacturonic acid solutions were nearly the same, the charge concentrations were similar for the different solutions. Based on the previous discussion, it is obvious that the charge concentration of a solution need not be the same as the cationic demand measured for the solution (both expressed in units of charge concentration, eq/L). However, for a polyelectrolyte solution, the measured cationic demand would be expected to be similar to the theoretical charge concentration of the solution, as calculated from the theoretical charge equivalence of the polyelectro-

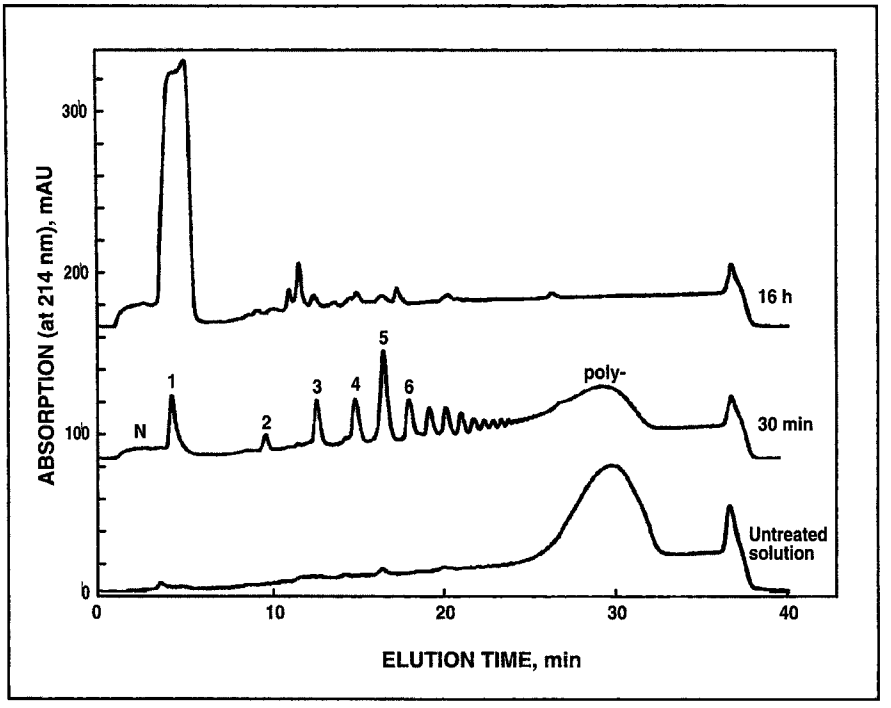
1. Cationic demand as a function of DP for 1-g/L solutions of mono-(DP 1), oligo-(DP 2–6), and poly-galacturonic acid (DP 20 and 130) as measured by polyelectrolyte titration



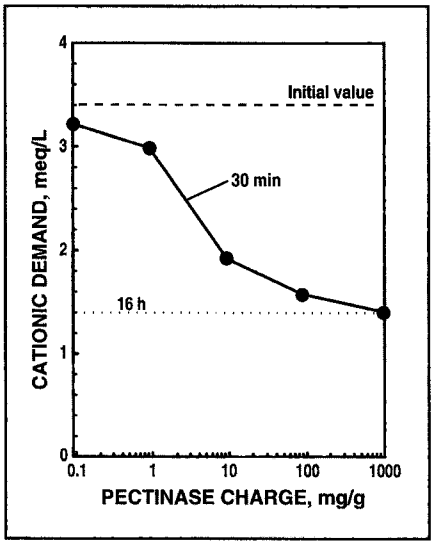
2. Cationic demand as a function of pectinase charge for 1-g/L solutions of Na-polypectate (DP 130)



3. Ion-exchange chromatography of untreated and pectinase-treated (30 min and 16 h at 10-mg/g pectinase charge) Na-polypectate solutions. Numbers represent DP of degradation products containing galacturonic acid; N represents neutral substances that are weakly retained by the Mono-Q column.



4. Cationic demand as a function of pectinase charge for filtrate from laboratory peroxide-bleached TMP. The dashed line represents the initial cationic demand of the untreated filtrate, and the dotted line represents the cationic demand of the filtrate, at highest pectinase charge, after 16 h of treatment.



lyte. For polygalacturonic acid, containing one charge per polymeric unit (176 g/mol per unit for galacturonic acid in polymeric form), the theoretical charge concentration of a 1-g/L solution would be

$$(1/176) \times 1000 = 5.68 \text{ meq/L}$$

The cationic demand measured for both Na-polygalacturonate solutions (1 g/L) was corrected by the factor

$$[(176 - 1) + 23]/176 = 1.125$$

to convert the cationic-demand values to that of polygalacturonic acid. The resulting calculated cationic demand for the two polygalacturonic acid samples deviated from the theoretical value by less than 10%, as seen in Fig. 1.

Cationic demand of pectinase-treated Na-polypectate solutions

A 1-g/L solution of Na-polypectate (DP 130) was treated with different pectinase charges. Cationic demand after 30 min of pectinase treatment was clearly dependent upon the pectinase charge, as seen in **Fig. 2**. Extending the time of pectinase treatment from 30 min to 16 h, at a pectinase charge of 10 mg/g, produced an additional decrease in cationic demand, suggesting that the decrease in cationic demand was due to depolymerization of the polygalacturonic acid.

Samples of the untreated solution and corresponding 30-min and 16-h pectinase-treated solutions (pectinase charge of 10 mg/g) were analyzed with ion-exchange chromatography (IEC). This technique is useful for monitoring the degradation of polygalacturonic acids and pectic substances *(34, 35)* and for preparative isolation of individual oligogalacturonic acids *(36)*. The untreated solution contained mainly polygalacturonic acid. **Figure 3** shows that galacturonic acid and oligogalacturonic acids were formed after 30 min of pectinase treatment. After 16 h pectinase treatment, nearly all of the original polygalacturonic acid was converted to galacturonic acid, resulting in a significant reduction in cationic demand. Figure 2 shows that the cationic demand after 16-h treatment was only 5% that of the original solution.

Pectinase treatment of laboratory-bleached TMP

Cationic demand for filtrate from laboratory peroxide-bleached thermomechanical pulp (TMP) was 3.4 meq/L. Pectinase treatment of the filtrate reduced cationic demand, especially at the highest pectinase charges. **Figure 4** shows that cationic demand after treatment at the highest pectinase charge for 30 min and 16 h was about 1.4 meq/L, approximately 40% of the value obtained for the untreated filtrate sample.

The pectinase treatment was also carried out on a laboratory-bleached TMP sample at 10% consistency. Samples containing dissolved and colloidal substances (DCS) were obtained from untreated and pectinase-treated bleached TMP. **Table I** shows that cationic demand of the sample decreased from 431 μeq/L to 248 μeq/L after pectinase treatment.

The increased total organic carbon (TOC) concentration for the DCS sample from pectinase-treated TMP represents a potential loss of 0.8% fi-

ber yield (assuming 40% carbon for the substances released from the fiber). The most abundant hemicelluloses comprising Norway spruce wood, and other softwood species, are the O-acetylgalactoglucomannans *(37)*. These are also the most abundant hemicelluloses present in DCS samples from unbleached TMP *(1)*. Direct analysis of the DCS monosaccharides, and the monomeric units comprising the DCS carbohydrates, revealed that most of the increase in TOC was probably due to the release of galactoglucomannans from the pulp fibers (Table I). The small increase in neutral monosaccharides—relative to the substantial increase in mannose, galactose, and glucose units comprising the DCS carbohydrates—suggests that the pectinase had an endo-hemicellulase side activity. Hemicellulase activity has been reported for the commercial pectinase used in this study *(38)*.

Because of the high ionic strength and the presence of hydrophobic substances, IEC could not be easily used to analyze the degradation products from pectinase treatment of the peroxide-bleached TMP sample. Monosaccharide analysis of the freeze-dried DCS, by direct silylation and gas chromatography (GC), showed that galacturonic acid increased from 2 mg/L to 42 mg/L following the pectinase treatment (Table I). This confirms that the polygalacturonic acid released from the TMP during peroxide bleaching was substantially degraded to galacturonic acid because of the pectinase treatment. Di- and oligo-galacturonic acids, possibly present in the DCS sample from the pectinase-treated TMP, were not detected in the GC analysis used for monosaccharides. The polygalacturonic acid released from the TMP in peroxide bleaching and present in the DCS sample accounted for about 5% of the organic DCS and as much as 50% of the potential "anionic trash."

Pectinase treatment of mill-bleached SGW

Carbohydrate analysis was also carried out on a laboratory-prepared filtrate from peroxide-bleached stone groundwood (SGW) from a pulp mill in southern Finland. Analysis showed that the most prevalent monomeric unit comprising the DCS carbohydrates was galacturonic acid. A SGW sample (5.5% consistency) taken from the same mill was treated with the pectinase at a charge of 0.5 mg/g o.d. pulp at 55°C and pH 5.1 for 30 min. Cationic demand of filtrate taken from the untreated SGW sample was 3.5 meq/L. After pectinase treatment, the cationic demand for the filtrate dropped to 1.8 meq/L, about 50% of the value for the untreated SGW filtrate.

Mill personnel have reported that increased amounts of cationic retention aid are needed to obtain satisfactory filler retention during intermittent periods of peroxide bleaching. Polyelectrolyte titration of the white water at various points throughout the system showed that increased cationic demand, possibly indicative of increased levels of "anionic trash," were due to the intermittent use of peroxide bleaching. The increased cationic demand and need for larger doses of cationic retention aid may be partly explained by the release of polygalacturonic acids from SGW during periods of peroxide bleaching. Because polyelectrolyte interactions are affected by ionic strength, part of the increase in the dosage of cationic retention aid and in cationic demand also may be attributable to the large amounts of electrolyte introduced into the papermaking system by the addition of bleaching chemicals.

I. Comparison of dissolved and colloidal substances in peroxide-bleached TMP before and after pectinase treatment.*

	Untreated	*Pectinase treated*
Cationic demand, μeq/L	**431**	**248**
TOC, mg/L	**368**	**400**
Monosaccharides, mg/L		
Neutral	12	18
Galacturonic acid	2	42
Total monosaccharides	**14**	**60**
Carbohydrates, mg/L		
Arabinose	10	11
Xylose	11	16
Mannose	23	46
Galactose	27	32
Glucose	27	30
Glucuronic acid	2	2
Galacturonic acid	48	57
Total carbohydrates	**148**	**194**

*TMP bleached in the laboratory and treated at 10% consistency

Potential application of pectinase treatment to papermaking

Preventing formation of complexes with cationic additives. The presence of polygalacturonic acids in the wet end of the paper machine will likely affect wet-end chemistry. These highly charged polysaccharides will likely complex with cationic retention/drainage aids, possibly reducing their effectiveness. Pectinase treatment can degrade polygalacturonic acids to lower-molar-mass oligomers and monomers, thereby preventing their complexation with the cationic additives.

The addition of Ca^{2+} and Al^{3+} will likely form insoluble complexes with the polygalacturonic acid. Both aluminum sulfate and calcium chloride have been used in laboratory techniques to precipitate polygalacturonic acids, selectively as a gel, from the initial dilute solution *(25)*. Recent work at this department has shown that colloidal substances originating from peroxide-bleached mechanical pulp are completely destabilized (aggregated) by the addition of $CaCl_2$ and $AlCl_3$ *(39)*. In the same study, it was shown that polygalacturonic acids were coaggregated with the colloidal substances (composed primarily of lipophilic extractives). Furthermore, the addition

of $CaCl_2$ and Na-polypectate (DP 130) to filtrate from unbleached TMP resulted in extensive coaggregation of the colloidal lipophilic extractives with the Ca-polypectate. In short, calcium and polygalacturonic acid can act together as a two-component flocculation system, thereby aggregating the colloidal substances present. This uncontrolled flocculation may produce undesirable effects in the papermaking process. Pectinase treatment prior to the introduction of the metal ions would prevent the formation of insoluble calcium or aluminum polygalacturonate.

It has also been observed in this laboratory that a cationic fixation aid, polydiallyl dimethyl ammonium chloride (poly-DADMAC), forms polyelectrolyte complexes with the polygalacturonic acids released from TMP in peroxide bleaching *(40)*. Using the same pectinase treatment as in the present study, it was shown that this complexation could be prevented and that the amount of fixation aid required to reach maximum flocculation of DCS (i.e., optimum polymer dose) was significantly lower than required for the untreated bleached suspension.

Effect on system ionic strength. Because polygalacturonic acid probably forms complexes with cationic papermaking polymers, the conversion of polygalacturonic acid to galacturonic acid will probably increase the amount of galacturonic acid circulating in the water system when steady-state conditions are reached. This probably will have little effect on the system's steady-state ionic strength because, prior to pectinase treatment, NaCl would be formed in the complexation of the cationic polymer and the Na-polygalacturonate. After enzyme treatment, Na-galacturonate would be formed, and the cationic polymer would be free to interact with other anionic charged polymers or surfaces. Furthermore, the amount of Na-polygalacturonate present in a peroxide-bleached TMP suspension at 1% consistency (about 50 mg/L) is rather small compared with the amount of Na-acetate and Na-formate (over 235 mg/L) *(1)* and the other simple salts formed upon neutralization of the residual bleaching chemicals with SO_2 (at least another 200–300 mg/L from the remaining sodium added in the bleaching chemicals). Even though enzyme preparations can contain large amounts of electrolyte, no significant increase in ionic strength of the DCS samples was detected following pectinase treatment.

Topics needing further study. The potential benefits, if any, of using this new treatment method for deactivating polygalacturonic acids will only be realized when mill-scale trials are carried out, and benefits may be specific for individual mills. The pectinase used in this study may be suitable for such trials. However, screening of all potential pectinase preparations and identification of their optimum reaction conditions, including the present enzyme, will be needed before mills can choose an appropriate pectinase for treatment of peroxide-bleached mechanical pulp. It may also be necessary to identify and isolate new pectinases that are more suitable to the conditions of modern mechanical pulp mills.

An ideal pectinase would efficiently degrade the polygalacturonic acids in the presence of residual SO_2 (used to acidify the pulp after bleaching) and work effectively at high temperatures (50–70°C). Cellulase and hemicellulase activities should be minimal to prevent loss of fiber yield. The potential yield loss measured in the present study, about 0.8%, is substantial and would probably be unacceptable for most papermaking operations. More optimum reaction conditions may prevent yield loss of such magnitude. If such side activities are unavoidable, fiber yield losses can be minimized by carrying out the pectinase treatment on fiber-free filtrate from the peroxide-bleached mechanical pulp. Recirculation of the enzyme back to the refiners (or stones) would likely denature the enzyme, resulting in its deactivation.

Conclusions

The cationic demand of a polygalacturonic acid solution can be decreased by depolymerizing the polygalacturonic acid through pectinase treatment. As much as 50% of the anionic polyelectrolytes, or potential "anionic trash," present in peroxide-bleached mechanical pulp suspensions are polygalacturonic acids, which represent only a small portion of the total organic dissolved and colloidal substances. Pectinase treatment can depolymerize the polygalacturonic acids, thereby preventing their complexation with cationic polymers. This treatment method may offer a new approach for managing the "anionic trash" released from mechanical pulp during peroxide bleaching.

Experimental procedures

Model compounds containing galacturonic acid

Solutions of the model compounds (1 g/L) were made in distilled water. Galacturonic acid (Fluka AG) and di- and tri-galacturonic acids (Sigma) were commercially available. Samples of di- through hexa-galacturonic acids were donated by the USDA (Philadelphia). Na-polygalacturonate was isolated from circulation water in a TMP peroxide bleach plant *(41)*. Using gel permeation chromatography, the DP of this sample was found to be about 20. A Na-salt of polygalacturonic acid—85–90% pure Na-polypectate (Sigma)—was also commercially available. The average DP for this polymer was about 130 *(41)*.

Measurement of cationic demand via polyelectrolyte titration

Cationic demand was measured using a Rank Brothers Model CA II charge analyzer utilizing streaming-current detection for endpoint determination. Polybrene—hexadimethrine bromide (Fluka AG)—was used as the standard cationic polyelectrolyte, and potassium polyvinylsulfate (KPVS), degree of esterification 91.9% (Wako

Pure Chemical Industries), was used as the standard anionic polyelectrolyte. Back titration was used to measure cationic demand as follows:

For 1-g/L solutions of the model compounds, 0.5 mL of each solution was diluted to 200 mL with distilled water in the titration vessel. Excess polybrene ($5x10^{-4}N$) was then added, thereby reversing the charge of the sample. The excess polybrene was titrated with KPVS ($5x10^{-4}N$), and the endpoint (i.e., the isoelectric point) was the dose of KPVS needed to neutralize the charge caused by the excess polybrene. The amount of excess polybrene added (usually 5–7 mL) was chosen so that the KPVS endpoint was between 2.5–6 mL. The cationic demand of the sample was determined according to the following relationship:

$$CD = [(PR) - KPVS]/2V$$

where

CD = cationic demand, meq/L

P = amount of polybrene, mL

R = ratio (usually about 1) of KPVS solution needed to ti trate 5 mL of polybrene solu tion

KPVS = amount of potassium polyvinylsulfate solution, mL

V = volume of the original sample.

Between three and five titrations were carried out for each sample. All titrations were performed at pH 6.5–7.

Pectinase treatments

The Na-polypectate solution was treated with a commercial pectinase (Pectinex™ Ultra SP-L, Novo Nordisk) produced from a selected strain belonging to the *Aspergillus niger* group *(38)*. Small amounts of the concentrated pectinase solution were diluted with distilled water, giving 10-mL pectinase solutions with concentrations between 100 g/L and 0.001 g/L. From each solution, a 1-mL sample was removed and thoroughly mixed with 100-mL aliquots of the Na-polypectate solution at 50°C. After 30 min at 50°C, the plastic bags containing the treated solutions were immersed in a hot water bath (80°C) for 5 min to stop the action of the enzyme. After cooling to room temperature, cationic demand for the initial solution and the six pectinase-treated solutions was measured according to the method described earlier. For the 10-mg/g pectinase charge, a 50-mL portion was allowed to react for 16 h, after which cationic demand was determined.

A TMP sample was peroxide bleached (3% peroxide on o.d. pulp) using an earlier reported method *(1)*. After acidification with SO_2 to pH ≈ 5, filtrate was sampled from the pulp by vacuum filtration with a Buchner funnel. Noncolloidal fibers and fines were removed from the filtrate by centrifugation. Aliquots of the filtrate (4 mL) were treated with different pectinase charges (0.2 mL) using the same general procedure as described previously. A blank treatment using 0.2 mL distilled water was also carried out. Cationic demand was determined using 0.5-mL aliquots of the blank and samples of pectinase-treated filtrate.

Another peroxide-bleached, and SO_2 acidified, TMP sample (10% consistency, 10 g o.d.) was prepared and treated with the pectinase by adding 10 mL of a 10-g/L solution of the pectinase to filtrate that was squeezed from the pulp into the corner of the bag containing the pulp (1 mg pectinase/g o.d. pulp). The filtrate was then kneaded thoroughly into the pulp to ensure effective mixing of pectinase within the pulp. The treatment was carried out for 30 min at 50°C, after which the bag containing the pulp was immersed into a hot water bath to stop the action of the enzyme. For comparison, an untreated bleached TMP sample (10 mL water added instead of the pectinase solution) was subjected to the same conditions as the pectinase-treated pulp.

Ion-exchange chromatography

Ion-exchange chromatography was carried out using a Mono Q HR 5/5 column (Pharmacia, Sweden), 1 mL bed volume in the Cl^- form, with a Hewlett–Packard model 1090A liquid chromatograph (dual solvent-delivery system). After loading the 2-mL injection loop with Na-polypectate solution (untreated or pectinase treated), the analysis was begun automatically by injecting the sample. The flow rate was 1 mL/min. After the sample passed through the column, a NaCl gradient was used to elute the mono-, oligo-, and poly-galacturonic acids from the cationically charged column. The elution was monitored at 214 nm. Solvent A was Milli-Q™ water, and Solvent B was 1*M* NaCl in Solvent A. The gradient used was 2% B (20m*M* NaCl) for the first 3 min after sample injection followed by a linear gradient up to 50% B (500m*M* NaCl) after 33 min. A 1-mL sample of Solvent B was used to regenerate the column for the next injection, which was followed by lowering the salt concentration back to the starting conditions (20m*M*) and equilibrating for at least 5 min. The mono- and oligo-galacturonic acid model compounds were used to assist in the identification of the peaks labeled in Fig. 3.

Preparation and analysis of DCS samples

Dissolved and colloidal substances (DCS) were sampled from the untreated and pectinase-treated TMP samples by diluting the pulp (10 g) to 1% consistency with distilled water, agitating for 3 h at 60°C, and centrifuging the resulting suspension for 30 min at about 500 *g* to obtain a fiber-free and fines-free supernatant containing the DCS *(1)*. Cationic demand was measured using 7-mL aliquots of the DCS samples. TOC, monosaccharides, and carbohydrates were analyzed as reported previously *(1)*. The pectinase solution was analyzed to determine its contribution to these values and, if necessary, to correct the values measured for the DCS from pectinase-treated TMP. ■

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