

Conversion of Agricultural Residues into Cation Exchange Materials

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SYNOPSIS

A series of cation exchange resins were prepared from some low-value agricultural residues. Carboxylate (maleate, succinate, and phthalate), phosphate, and sulfate groups were incorporated onto the complex polysaccharide matrix of oat hulls, corn cobs, and sugar beet pulp. Standard reaction conditions were established, using cellulose as the model polysaccharide. The magnitude of functional group incorporation, under standard conditions, was taken as a measure of the reactivity of the agricultural residues studied. In general, the order of reactivity was sugar beet pulp > corn cob > oat hull. The unsubstituted and the functionalized agricultural residues were tested for their potential ability to remove cations from waste water discharges. The capability of these materials to remove cations from waste waters was estimated from their calcium binding capacity. The calcium binding capacities of the resins prepared from the agricultural residues varied from around 559–3466 $\mu\text{equiv/g}$. © 1996 John Wiley & Sons, Inc.*

INTRODUCTION

Large amounts of low-value, residual materials are produced during the harvesting and processing of food and industrial crops. For example, 58% of the total solid material produced during the harvesting of corn is low-value lignocellulosic residue or waste.¹ During processing, additional residues are produced that can cause expensive disposal problems. The possibility of converting some of these residues into cation exchange resins that might have utility in water purification and removal of toxic metals from waste streams has been investigated. The advantages are twofold. By adding commercial value, one can simultaneously eliminate a possible pollution or disposal problem caused by these residues and increase the value of a crop to the farmer or processor.

A harvest residue produced from corn (i.e., ground-up cobs), a milling residue (i.e., oat hulls), and a processing residue (i.e., sugar beet pulp) were investigated as possible candidates for conversion into ion exchangers. For this sort of use, residues may be considered resources for commercial development rather than environmental problems.

Large quantities of these materials are potentially available from crops harvested in the United States. It is estimated that 222 million tons of corn were produced in 1990.² The yield of corn cobs was in excess of 40 million tons.¹ Most of this material was ground up during harvesting by the combine and returned to the soil. Small amounts were collected and used as abrasives and adsorbents. Oats harvested in 1990 came to 5.7 million tons.² The hull is approximately 25% of the total (1.43 million tons).³ Because of its large pentosan content (29%), much of it is used to prepare furfural by cyclodehydration.³ The sugar beet harvest in 1990 netted 27.6 million tons.² Of this, 5% was waste pulp (1.38 million tons).⁴ Currently, almost all of the pulp is dried and pelleted for animal feed. This is a low-value (\$70/ton) product made from an energy-intensive process.

Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by the USDA implies no approval of the product to the exclusion of others that may also be suitable.

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Agricultural residues are mixtures of complex polysaccharides and lignin. Some of the isolated components of these mixtures (i.e., cellulose and starch) have increased value when new functionality is added. For example, cationic and carboxymethylated starches and celluloses have many industrial and commercial uses. By applying the same or similar methodology to the unprocessed residues, useful products could be produced. These products would be less costly because the isolation and purification steps would be eliminated. A potential waste disposal problem would be minimized because these residues would now have some commercial utility. In this investigation, modified literature methods were used for the incorporation of sulfate, phosphate, succinate, phthalate, and maleate (Fig. 1) into the complex polysaccharide matrices of the aforementioned crude agricultural residues.⁵⁻⁹ The potential usefulness of these derivatized residues as cation exchange agents was evaluated. Calcium ion binding capacities of these modified materials were measured, and some were additionally evaluated for their ability to remove lead from a standard water solution.

MATERIALS AND METHODS

Materials

Sugar beet fiber (SBF, DuoFiber), obtained from American Crystal Sugar Co. (Moorhead, MN), is a sugar beet pulp product that has been treated with SO₂ to reduce color formation during drying. Residual oil was extracted with isoamyl alcohol. Particle size covered a range from 0.42 to 2.0 mm. The sample of corn cob (CC) obtained from The Anderson's (Maumee, OH) was from the woody part of the cob. Samples covering two different ranges of particle sizes were evaluated. Grit-o'cob 814 and Grit-o'cob 1420 have particle size distributions of 80% 1.4–2.0 mm and 90% 0.85–1.4 mm, respectively. Oat Hull (OH) was an unsieved sample containing stringy particles from 0.1 to 3.3 mm in length. Chemical reagents were obtained from Aldrich Chemical (Milwaukee, WI) and used without further purification [cellulose powder (20 μm) maleic anhydride, phthalic anhydride, succinic anhydride, phosphorus oxychloride, chlorosulfonic acid, pyridine, toluene, and methylene chloride].

Methods

Maleate

Ten grams of the dried residue were suspended in 50 mL of dried pyridine. Maleic anhydride (3 g) dis-

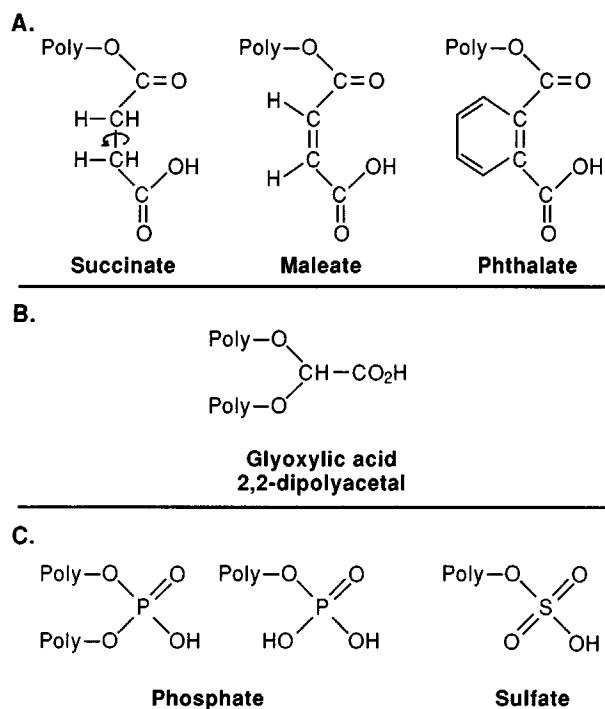


Figure 1 A schematic depicting the spatial relationships of the functional groups grafted onto the polysaccharide (poly) backbone.

solved in 20 mL toluene was added to the stirred suspension over 2 min and heated at 105°C for 45 min. The suspension was cooled and then poured into a beaker containing 250 mL of ice water. The solid material was filtered and then successively washed with 50 mL each of 0.1N HCl, water, and methanol and then air dried overnight.

Succinate

Ten grams of the dried residue were suspended in 50 mL of dried pyridine. Succinic anhydride (5 g) was added portionwise over 2 min to the stirred suspension and then heated at 115°C for 1 h. The mixture was cooled and then poured into ice water. The residue was filtered and successively washed, and dried as described previously.

Phthalate

Ten grams of the dried residue were suspended in 50 mL of dried pyridine. Phthalic anhydride (7.5 g) was added portionwise over 2 min to the stirred suspension and then heated at 115°C for 75 min. The mixture was cooled and then poured into ice water. The residue was filtered and successively washed, and dried as described previously.

Table I Calcium Binding Capacities of Corn Cob, Oat Hull, Sugar Beet Pulp, and Cellulose and Their Functionalized Derivatives

Added Functionality	Corn Cob (814)	Oat Hull	Sugar Beet Pulp	Cellulose
None	120 ^a	110	520	0
Phthalate	1210	692	1315	1152
Succinate	1393	1282	3272	2403
Maleate	722	174	559	707
Phosphate	798	1169	2586	2461
Sulfate	1636	1093	3466	4123 ^b
Glyoxylic acid	203	139	437 ^c (1242) ^d	265

^a Calcium binding capacity $\mu\text{equiv/g}$.

^b Water soluble.

^c Amide from ammonolysis.

^d Acid by hydrolysis.

Glyoxylic Acid Acetal

Five grams of sugar beet pulp were suspended in 25 mL of glyoxylic acid. Concentrated hydrochloric acid (5 mL) was added to the suspension, which then was shaken for 2 h. The solid mass was dispersed in 100 mL alcohol and filtered. It was resuspended in a cooled solution of alcohol (150 mL) containing concentrated ammonium hydroxide (15 mL). The suspension was filtered and the solid material was air dried.

Phosphate

Ten grams of the dried residue were suspended in 100 mL of dried pyridine. Phosphorus oxychloride (10 mL) in 50 mL methylene chloride was added dropwise over 2–5 min to the stirred, cooled suspension and then heated at 115°C for 120 min. The mixture was cooled and then poured into ice water. The residue was filtered, successively washed with 0.1N HCl, water, and methanol, and then dried as described previously.

Sulfate

Ten grams of the dried residue were suspended in 100 mL of dried pyridine. Chlorosulfonic acid (10 mL) in 50 mL methylene chloride was added dropwise over 2–5 min to the stirred, cooled suspension and then heated at 115°C for 120 min. The solution was cooled and then poured into ice water, filtered, successively washed with 0.1N HCl, water, and methanol, and then dried as described previously.

Drying of Agricultural Residues

Residues were dried *in situ* by azeotropic distillation with dry pyridine (2 mL pyridine/g of residue).

Calcium Binding

The method used was that described by Laszlo and Dintzis.¹⁰

RESULTS AND DISCUSSION

Unsubstituted Agricultural Residues

The ion binding potentials of native and substituted residues can be estimated from their calcium binding ability.¹⁰ The native materials have inherent calcium binding capabilities in the following order: sugar beet > corn cob > oat hull > cellulose (Table I). The differences in binding capacities are related to differences in glycan composition¹¹ (Table II).¹² Crude polysaccharides in corn cobs, oat hull, and sugar beet pulp contain different ratios of two types of functional groups which differ in their abilities to bind cations. The carboxyl group has a strong affinity for cations whereas the hydroxyl group has a weak affinity. Pure cellulose contains only hydroxyl groups, and its binding ability is dependent on the pH at which the binding is performed.¹³ At neutral or acidic pH, the ability of pure cellulose to bind cations is minimal. Some cellulose preparations, however, have appreciable ion binding capacity, which is due to the manner in which the cellulose is prepared. Various types of pretreatment can oxidize the terminal hydroxyl to a carboxyl with an accompanying increase in cation binding capacity. Corn cob and oat hull have binding capacities higher than cellulose due to a small quantity of pectinlike material (3%). Sugar beet has an appreciably higher binding capability due to the large amount of native pectin (25%), which has free carboxyl groups. Because carboxylate and alcoholate groups are hard bases, one would ex-

Table II Proximate Percent Compositions of Agricultural Residues

	Corn Cob ^a	Oat Hull ^b	Sugar Beet Pulp ^c
Cellulose	41	38	20
Hemicellulose	36	48	32
Pectin	3	3	25
Lignin	6	11	4

^a Benson and Pearce in *Corn*.⁷

^b V. F. Rasper in *Dietary Fibers*.⁸

^c Data sheet for DuoFiber, American Crystal Sugar Co., Moorhead, MN.

pect both to form strong complexes with calcium, a hard acid. Hard acids prefer to coordinate to hard bases, and soft acids prefer to coordinate to soft bases.¹⁴ However, their relative abundances at moderate pH are vastly different, as can be deduced from their pK_a values: galacturonic acid carboxyl $pK_a = 4.5$, glycerol hydroxyl $pK_a = 14.2$. Most of the galacturonic acid in sugar beet pulp pectin is present as a methyl ester (70% methyl) and cannot form an ionic bond with cations.¹⁵ Consequently, the calcium ion binding capacity listed in Table I does not indicate the total potential binding capacity of the residue. For example, treatment of sugar beet with mild base removes the methyl groups and converts the ester into the free acid, thereby raising the calcium exchange capacity to 1200 $\mu\text{equiv/g}$. As none of the chemical treatments described in this article would be expected to remove the methyl group, a comparison of the binding capacities of these derivatized materials to the native materials is justified. Thus, any increase in binding capacity of the derivatized agricultural residue is due to the new functionality. An exception is the acetal prepared from glyoxylic acid. The addition of ammonium hydroxide during the workup of the reaction mixture removes the methyl group from sugar beet pectin and transforms the ester either into an amide (ammonolysis)¹⁶ or an acid (hydrolysis). The pectin amide and the starting pectin ester should have the same calcium binding values. The product obtained upon adding ammonium hydroxide to a suspension of the residue from the glyoxylic acid reaction had a calcium binding value of 1242, while the product obtained by adding the residue from the glyoxylic acid reaction to a cooled solution of ammonium hydroxide in alcohol had a binding value of 437 (Table I). These values are similar to the calcium binding values of the native sugar beet after and before hydrolysis. Apparently, the former reaction condition favored hydrolysis while the later favored ammonolysis. These experimental values indicate that incorporation of glyoxylic acid into sugar beet pulp did not

occur. The binding values for the other treated residues indicate minimal incorporation of glyoxylic acid (Table I).

Derivatized Agricultural Residues

Addition of phosphate, sulfate, succinyl, maleyl, and phthalyl ester groups onto corn cob, sugar beet, oat hull, and cellulose increased the abilities of these materials to act as cation exchangers. The calcium binding capacities of the substituted and untreated residues are listed in Table I. The number of groups appended to a residue is directly related to its capacity to act as a cation exchanger. The differences between the calcium binding values for native and substituted materials is an indication of the degrees to which functionality has been added. Some generalizations can be made from the calcium binding values in Table I. The results for any one reagent group are comparable because the reaction conditions and reagent ratios developed for cellulose were duplicated for the residues.

The highest degrees of substitution (sulfation) were found with chlorosulfonic acid, a relatively small molecule having maximum accessibility to the inner matrix and the most reactive reagent. A series of cellulose sulfates was prepared by incrementally increasing the amount of chlorosulfonic acid. Low levels of sulfate incorporation gave water-insoluble products, whereas high levels of incorporation gave water-soluble polymers. The water-soluble cellulose sulfate reported in Table I was prepared by increasing the amount of chlorosulfonic acid to 15 mL. A comparable series of experiments was not tried with the agricultural residues.

The low calcium binding values obtained with oat hull as compared to the other residues is due to its compact, rigid structure (Fig. 2) and the relatively large amount of lignin. The tightly bound three-dimensional matrix limits accessibility of the reagent to the polysaccharide hydroxyl groups.

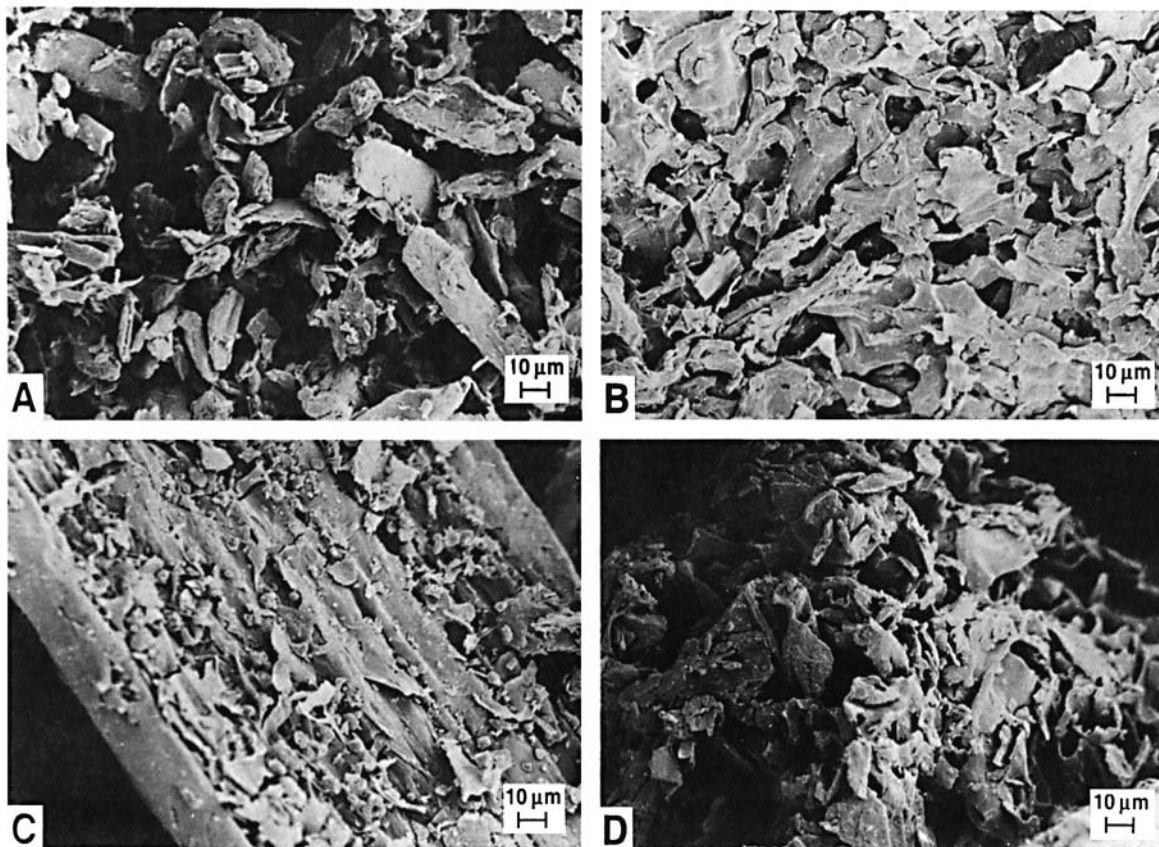


Figure 2 SEM micrograph of (a) cellulose, (b) corn cob, (c) oat hull, (d) sugar beet pulp.

An anomaly is noted when comparing sulfation and phosphorylation of oat hulls (Table I). The calcium binding capacity of the sulfate is slightly less than the calcium binding capacity of the phosphate. This is opposite of what is expected. Chlorosulfonic acid is a more reactive reagent than phosphorus oxychloride and would be expected to incorporate a greater number of ionizable groups into the polysaccharide. Normally, chlorosulfonic acid will react with a hydroxyl group on a polysaccharide to form a half ester with one ionizable proton. However, because of the large amount of lignin in oat hull, chlorosulfonic acid now has a competing reaction pathway: chlorosulfonylation of the aromatic groups in the lignin.¹⁷ The reactive chlorosulfonyl group which forms will react with one of the many hydroxyls on the polysaccharide to form an ester crosslink (a nonionizable group). This would be the expected sequence of reactions since chlorosulfonic acid was added in a manner to promote crosslinking (i.e., small amounts of a multidentate reagent incrementally added to a large amount of a substrate having multiple reaction sites). Phosphorus oxychloride would be expected to singly crosslink two hydroxyl

groups for a similar reason. The remaining chloride will be hydrolyzed during the reaction workup, giving a crosslinked product with one ionizable hydrogen (starch,⁷ cellulose¹⁸).

With the anhydrides, the substitution level (calcium binding ability) would be expected to parallel the molecular size of the reagent: maleate > succinate > phthalate. Maleic anhydride, being the smallest molecule and thus having the greatest accessibility to the inner matrix, should have the highest calcium binding level. However, one finds that maleate has the lowest degree of substitution. This anomaly is not caused by low reactivity of maleic anhydride with the residues, but rather by a loss of maleic anhydride to a competing reaction with the solvent pyridine. Succinic and phthalic anhydrides, which do not react vigorously with pyridine, follow the expected pattern.

With each residue, the increase in calcium binding over and above the value of the native material is due to incorporation of new functionality. This increase is generally greatest with sugar beet pulp and cellulose. The reasons are twofold. The large sugar beet pulp particles have an open, porous structure

Table III Comparison of Lead and Calcium Binding Capacities of Substituted Agricultural Residues

Agricultural Residue ^a	Lead Binding Capacity (μ equiv/g)	Calcium Binding Capacity (μ equiv/g)	Ca/Pb Selectivity Ratio
Corn cob (phosphate)	838	798	0.95
Oat hull (sulfate)	500	1093	2.19
Sugar beet	422	1242	2.94
Sugar beet (phthalate)	948	1315	1.39
Oat hull (succinate)	885	1282	1.45
Oat hull (maleate)	106	174	1.64

^a Substituted agricultural residues in parentheses.

(large surface area) and thus a greater number of hydroxyl groups are exposed and available for reaction with the reagents. Scanning electron microscopy (SEM) micrographs of this porous structure and the ability to swell are in accord with this hypothesis. Cellulose, by contrast, has a compact structure (Fig. 2). Nevertheless, the sample has a large surface area and many exposed hydroxyl groups by virtue of the small (20 μ m) particle size.

Selectivity

The hydroxyl functionality on all of these residues is amenable to substitution with a wide variety of electrophilic reagents. Multiple functional groups may be placed on the same repeating unit or on one in close proximity. This plethora of reactive sites may lead to some degree of selective rejection of cations having large ionic radii due to steric hinderance factors or selective adsorption due to polydentate bonding. The organic derivatives prepared from these agricultural residues were succinate, phthalate, and maleate half esters. Phosphate and sulfate groups were appended to the polysaccharide without the use of spacers. The sulfate monoester, a half ester, has the smallest size and is better able to reside in the interior of the biopolymer matrix. The phosphorous oxychloride can react at a single site and the product can remain as a dianion, or it can react with two sites on biopolymer backbones, crosslink them, and result in only a monoanion to react with a cation.^{7,18} Slow incremental additions of reagents should lead to the latter, while reverse addition should lead to the former.

In the present examples, the objective is to improve cation binding characteristics of a group of agricultural residues. Consequently, these derivatives were selected as models because they were expected to give derivatized residues with slightly different topographies. The spacial relationships between the vicinal carboxyl groups on phthalate and

maleate are fixed in space due to the double bond. The vicinal carboxyl groups of succinate are separated by a single bond and are free to rotate (Fig. 1), which allows more flexibility in accommodating the spacial requirements of larger cations. The initial ion-ion bond between the cation and the polymer can be reinforced by an ion-dipole interaction between the cation and the carbonyl of the ester carboxyl attached to the polymer. Ion-dipole interactions between a cation and oxygens from the many free hydroxyls can occur with any of these derivatives.

The derivatized agricultural residues displayed a preference for calcium over lead (Table III), which is the reverse of what occurs with the sulfonated styrene divinylbenzene resins.¹⁹ A series of derivatized polysaccharides was tested for ability to bind calcium and lead by stirring 50–200 mg of a residue in a standard solution containing calcium or lead salts and then analyzing an aliquot for the residual cation. The difference between the starting concentration of cation (calcium or lead) and its final concentration is a measure of a polymer's ability to bind that cation. The derivatized residue had a higher capacity for calcium than for lead in all the samples tested except for phosphorylated corn cobs. The reduced ability to bind lead probably is due to both steric and electronic effects. Lead has a larger ionic radius than calcium (1.20 Å vs. 0.99 Å), which reduces its access to functional groups in the interior matrix. This result is in agreement with Boyd et al.,²⁰ who concluded that ion exchange adsorption affinities are determined chiefly by the magnitude of the charge and the hydrated radius of the ion in solution. In addition, lead is a semihard acid and is held less tenaciously by these substituted residues than calcium, which is a hard acid. The anomalous behavior of corn cob indicates something unique about the phosphate derivative. Additional studies will be required to define precisely the cause for lack of selectivity with this sample.

From the selectivity ratios (Table III), it is obvious that subtle changes in topography caused by the presence or absence of a double bond had little effect on selectivity or binding ability.

This study has shown that such complex glycan-lignin mixtures as oat hull, corn cobs, and sugar beet pulp can be converted into composite cation exchange resins. It is not necessary to extract the pure components (starch, cellulose, hemicellulose, and lignin) in order to prepare a cation resin. The exchange capacities of these new materials (Table I) compare favorably with commercially available phosphorylated cellulose (Cellex-P, 850 $\mu\text{equiv/g}$),²¹ carboxymethyl cellulose (Cellex-CM, 470 $\mu\text{equiv/g}$),²¹ and sulfoethylcellulose (Servacel SE 23-cellulose, 250 $\mu\text{equiv/g}$).²²

Even though the crude materials (except for the sulfate) are not competitive in terms of exchange capacity with the styrene-divinylbenzene-type resins (Dowex-50, 5100 $\mu\text{equiv/g}$), they offer the advantage of being biodegradable and may offer other advantages in terms of selectivity.

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