Crop Residues as Ion-Exchange Materials. Treatment of Soybean Hull and Sugar Beet Fiber (Pulp) with Epichlorohydrin to Improve Cation-Exchange Capacity and Physical Stability

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SYNOPSIS

Ion exchange systems for the treatment of process water or wastewater may benefit by the use of inexpensive, disposable exchange materials before, or in place of, conventional regenerable exchange resins. Various agricultural by-products have been proposed as suitable exchangers for this role, but they generally fail to have adequate capacity and physical stability for most applications. Two by-products, soybean hull and sugar beet fiber, were found to have enhanced cation-exchange capacity and stability upon treatment with epichlorohydrin and base. Exchange capacity was determined by measuring calcium binding. Physical stability was judged by three different aqueous extraction regimens. The most efficacious and economical reaction conditions found were: soybean hull and sugar beet fiber hydrated with water at a water-to-solids ratio of 6.4 : 1 and 8 : 1 (v/w), respectively, and epichlorohydrin applied at a 0.3 : 1 (v/w) ratio, for 6 h at room temperature. The resultant cross-linked materials had cation-exchange capacities of approximately 0.9 (soybean hull) and 1.3 (sugar beet fiber) meq/g dry weight. These epichlorohydrin-treated agricultural by-products may serve as cost-effective, multivalent-cation exchangers. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Ion exchange resins are broadly employed for treatment of process water and wastewater. Commercially available synthetic resins provide a wide selection of ion selectivities and performance characteristics such that most applications can be cost-effectively addressed. Because of their relatively high cost and excellent durability, synthetic resins are regenerated repeatedly. However, the capital expenditure requirements and waste volumes associated with resin regeneration may be undesirable in some applications. In other instances, resin fouling or poisoning may be a problem. Thus, low-cost, single-use exchange resins can be usefully employed, either as stand-alone systems or precoats to regenerable resin beds.[1]

Numerous by-products of agricultural crop production and processing have been examined for potential use as inexpense adsorbents.[2-6] The native exchange capacity and general sorptive characteristics of these materials derive from their constituent polymers (in approximately decreasing order of abundance): cellulose, hemicellulose, pectin, lignin, and protein. Although shown to be effective adsorbents for a wide range of solutes, particularly divalent metals cations, crop residues suffer from at least two major drawbacks: low exchange or adsorption capacity, and poor physical stability (i.e., partial solubility). These two problems tend to go hand-in-hand. The constituent polymers most readily ex-

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tracted are generally also the ones bearing most of the adsorption sites.

Strategies developed to correct these problems include chemical modification, co-polymerization, and cross-linking.[7] However, the additional processing increases cost so that the derivatized agricultural residue is no longer inexpensive.

This report describes the treatment of two widely available agricultural by-products, soybean hull and sugar beet fiber, with epichlorohydrin to produce cation-exchange materials with increased capacity and physical stability. The procedure is facile and economical.

EXPERIMENTAL

Materials

Soybean hull (SH), 18–30 mesh, was obtained from Lauhoff Grain Co. (Danville, IL) and sugar beet fiber (SBF, Duofiber) was obtained from American Crystal Sugar Co. (Moorhead, MN). SBF is a beet pulp product that has been treated with SO_2 to reduce pigment formation during drying, and extracted with isoamyl alcohol to remove lipids. Epichlorohydrin (1-chloro-2,3-epoxypropane) was used as received from Aldrich Chemical Co. (Milwaukee, WI).

Preparation of Cross-linked SH and SBF

SH and SBF were derivatized starting with the materials in their as-received state. SH and SBF moisture contents were 10 and 25%, respectively. Reactions were conducted on 20 g SH (18 g dry weight) and 22 g SBF (16.5 g dry weight). Two different reaction conditions were employed in cross-linking SH and SBF, which are referred to herein as the full hydration and minimal hydration procedures. Both procedures were conducted at room temperature. For the full hydration procedure, SH and SBF were sufficiently hydrated (with water, epichlorohydrin, and base) to permit continuous mechanical stirring in a 3-neck, 500-mL round bottom flask, while the minimal hydration reaction mixture remained unstirred after initial mixing of reactants in a 400-mL beaker. For the fully hydrated reaction conditions, the SH reaction mixture received 160 mL of water, 24 mL of 5 N NaOH, and varying amounts of epichlorohydrin, while the SBF reaction contained 225 mL of water, 35 mL of 5 N NaOH, and varying amounts of epichlorohydrin. The SH or SBF, water, and epichlorohydrin were stirred 1–

2 h before the addition of base to initiate the reaction. Reaction time was varied. For the minimally hydrated reaction conditions, the SH mixture contained 100 mL of water, 15 mL of 5 N NaOH, and epichlorohydrin; the SBF reaction mixture contained 110 mL of water, 20 mL of 5 N NaOH, and epichlorohydrin. The SH or SBF, water, and epichlorohydrin were contacted as a stiff slurry 2 h before base addition. Reactions were terminated 6 h after base addition.

For both procedures, reactions were terminated by dilution with ethanol, followed by isolation of the insoluble products by filtration with either hardened cellulose paper or glass microfiber paper. Filtrates were dried under vacuum (25°C). Recovery of solids by this procedure was quantitative with respect to the SH or SBF starting material.

Characterization

All characterizations were conducted with the materials starting in the protonated form, free of other exchangeable cations, and dry. SH or SBF (5–10 g, untreated or epichlorohydrin treated) were suspended in 500 mL of water and titrated to pH 2 by the addition of dilute HCl. After equilibration for 2 h, solids were collected by filtration, washed successively with water and ethanol, then dried under vacuum (25°C).

Cation-Exchange Capacity Measurement

Determination of cation-exchange capacity of SH and SBF materials was based upon Ca^{2+}-binding ability. Samples (100–200 mg) were equilibrated for 2 h in 100 mL of 2.0 mM 3-[N-morpholino]propanesulfonic acid (Mops)/NaOH (pH 7.2) buffered solution containing 2.0 mM $CaCl_2$. Solution pH was readjusted to 7.0–7.2 by addition of small aliquots of approximately 1 N NaOH after the first hour of equilibration. After the equilibration period, a 5-mL aliquot of sample solution was filtered (0.45-μm pore size, polyvinylidene difluoride membrane filter). Calcium concentration (free Ca^{2+}) in the filtrate was measured colorimetrically with tetramethylmurexide (Sigma Chemical Co., St. Louis, MO) following the method of Ohnishi.[8] The difference between the initial and final Ca^{2+} concentrations was taken as a measure of total binding capacity of the material, assuming a stoichiometry of two exchange sites per Ca^{2+} bound. All exchange capacity measurements were made in triplicate, and are reported as microequivalents per gram dry weight of exchanger material.

Thermostability Tests

Three test procedures were employed to measure the enhancement of SH and SBF structural/compositional stability caused by cross-linking. The first procedure followed the method of Robertson and Van Soest,[9] with modifications described by Van Soest et al.,[10] for the measurement of neutral detergent fiber (NDF) content. This extraction method entailed treatment of the material with heat-stable α-amylase at 50°C for 1 h, followed by boiling for 1 h in a borate/phosphate-buffered solution containing 50 mM EDTA and 3% (w/v) sodium dodecyl sulfate. The recovered insoluble residue is termed the NDF fraction of the material. NDF measurements were made on duplicate 1-g samples. The second test procedure entailed soxhlet extraction of 1-g samples with water for 24 h (approx. 50 cycles) and measurement of the retained mass after drying. Samples were held at 75–80°C in the extraction thimble. Soxhlet treatments were performed in triplicate. The third test procedure consisted of treating the materials (1 g) in 100 mM sodium borate (100 mL), pH 9.1, for 1 to 9 days at 90°C in a shaker water bath. The weight of recovered insolubles constituted a measure of the thermostability of the sample. These measurements were made in triplicate. After each of the three tests, the ion-exchange capacity of the recovered residues was determined as described above.

Table I Comparison of Untreated and Epichlorohydrin-Treated Soybean Hulls and Sugar Beet Fiber: Neutral Detergent Fiber and Ion-Exchange Capacity

Material[b]	NDF[c] (%)	Exchange Capacity (μeq/g)[a] Before NDF Treatment	Exchange Capacity (μeq/g)[a] After NDF Treatment
Soybean hull			
Untreated	74	650 ± 10	270 ± 10
Cross-linked	96	850 ± 30	830 ± 20
Sugar beet fiber			
Untreated	76	670 ± 80	600 ± 40
Cross-linked	96	1220 ± 20	1320 ± 150

[a] Mean and one standard deviation of three determinations.
[b] Cross-linked: fully hydrated protocol, 14 mL epichlorohydrin, 20 h reaction time; untreated: original materials (no base or epichlorohydrin).
[c] Neutral detergent fiber treatment, mean of two determinations.

Table II Mass Recovery and Ion-Exchange Capacity After Soxhlet Extraction of Untreated and Epichlorohydrin-Treated Soybean Hulls and Sugar Beet Fiber

Material[a]	Mass Recovery (%)	Ion-Exchange Capacity[b] (%)
Soybean hull		
Untreated	69 ± 1	20 ± 3
Cross-linked	84 ± 2	73 ± 6
Sugar beet fiber		
Untreated	55 ± 2	63 ± 15
Cross-linked	70 ± 3	70 ± 3

[a] Cross-linked: fully hydrated protocol, 14 mL epichlorohydrin, 20 h reaction time; untreated: original materials (no base or epichlorohydrin).
[b] Mean and coefficient of variation of the ion-exchange capacity of insoluble residue recovered from soxhlet extraction. Residue ion-exchange capacity is represented as a percentage of the initial (prior to extraction) capacity (i.e., 100× residue/initial). See Table I (column 3) for the initial exchange capacities of these materials. Coefficient of variation was calculated as described by McFeeters and Armstrong.[11]

Swelling Volume Measurement

Determination of the swelling volume of both untreated and cross-linked SH and SBF was conducted in 100 mM sodium borate buffer, pH 9.1, at 25°C. Samples (0.5 g) were fully hydrated for 20 h in graduated conical centrifuge tubes containing excess buffer solution, then centrifuged for 10 min in a swinging bucket rotor (50 × g). Measurements of packed volume were made on duplicate samples. Swelling volume was calculated by dividing the packed volume (mL) by sample dry weight (g).

RESULTS

Cross-Linking Effects on Stability

SH and SBF have modest cation-exchange capacities, approximately 650 μeq/g, in their native state (Table I). A substantial fraction of mass and exchange capacity is extracted by various aqueous treatments. NDF treatment removed a quarter of SH mass and reduced the exchange capacity of the remaining insoluble material by more than half (Table I). SBF mass was solubilized to the same extent as SH mass by NDF treatment, but the remaining insoluble material had nearly the same exchange capacity as the untreated material (Table I). Soxhlet extraction of SH resulted in a mass recovery similar to that of NDF treatment, but had a

greater effect than NDF treatment on exchange capacity (Table II). SBF lost more mass with soxhlet treatment than NDF treatment (cf. Tables I, II), and the material remaining after soxhlet extraction had an exchange capacity substantially lower than the original untreated SBF (Table II). These treatments demonstrated the general lability of unmodified SH and SBF under a variety of conditions.
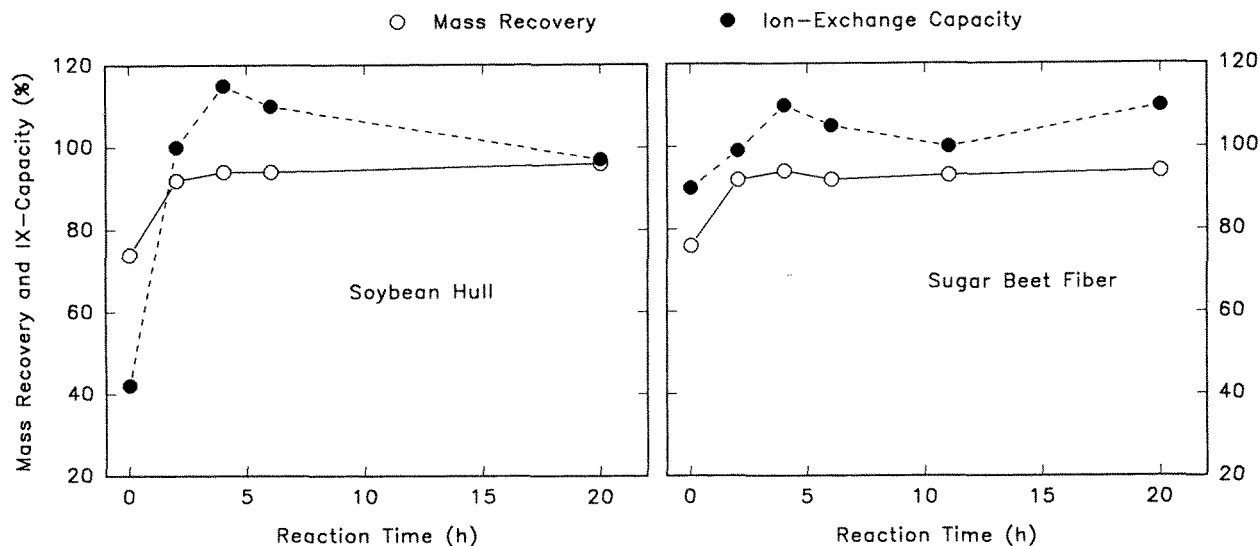
Crosslinking with epichlorohydrin following the full hydration procedure (described in Experimental) eliminated the losses of mass and exchange capacity from SH and SBF incurred by NDF treatment (Table I). Stability improvement by epichlorohydrin treatment was less dramatic when tested by soxhlet extraction (Table II). Epichlorohydrin treatment provided an additional benefit of increasing the exchange capacities of SH and, particularly, SBF (Table I), presumably by base-catalyzed hydrolysis of carboxymethylester groups in the pectin fractions.

The improvement in physical stability brought about by cross-linking with epichlorohydrin was further examined by subjecting untreated and cross-linked SH and SBF to extended periods at an elevated temperature. One-day incubation at 90°C in sodium borate buffer (pH 9.1) reduced SH mass and exchange capacity by about 35%, whereas epichlorohydrin-treated SH retained more than 90% of its mass and exchange capacity (Fig. 1). SBF lost half of its mass and almost one-fourth of its exchange capacity in the first day under these conditions, but cross-linked SBF lost only 10% of its mass and the exchange capacity loss was negligible (Fig. 1). Continued incubation resulted in increased solubilization of all samples. Unmodified SH and SBF lost 45–70% of their mass and 75% of their exchange capacity after 9 days at 90°C in sodium borate buffer (pH 9.1). The cross-linked SH and SBF mass and exchange capacity losses were 20% (mass) and 30% (capacity) after 9 days. Thus, epichlorohydrin treatment brought about a substantial improvement in stability, as determined by this test procedure. Addition of sodium azide (0.2% w/v) to the incubation solution (sodium borate) to prevent potential microbial activity did not alter mass and capacity losses (data not shown). This implies that only thermal degradation of constituent polymers was
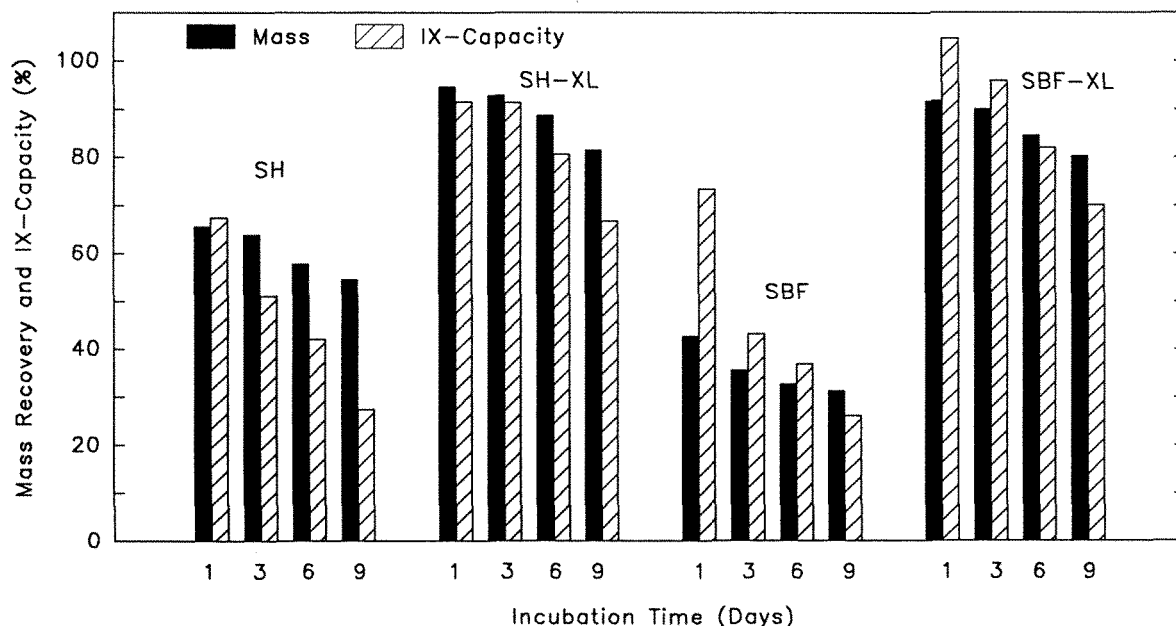
Figure 1 Effect of extended treatment at elevated temperatures on mass recovery and ion-exchange (IX-) capacity. Samples were incubated 1–9 days at 90°C in sodium borate buffer (pH 9.1). The mass recovery is expressed as a fraction of the original sample weight (1 g). The exchange capacity is expressed as the ratio of the recovered material to the unincubated material exchange capacities. Samples: soybean hull, not cross-linked (SH); sugar beet fiber, not cross-linked (SBF); epichlorohydrin-cross-linked soybean hull (SH-XL); and epichlorohydrin-cross-linked sugar beet fiber (SBF-XL). Cross-linked samples were treated with 14 mL of epichlorohydrin for 20 h, using the fully hydrated reaction conditions (see Experimental).

Figure 2 Effect of reaction time with epichlorohydrin on extent of cross-linking. Soybean hull and sugar beet fiber were treated with 14 mL of epichlorohydrin for 2–20 h under fully hydrated reaction conditions. The zero reaction time samples were not treated with epichlorohydrin or base. The effectiveness at each reaction time was determined by measuring the NDF fraction (mass recovery) and exchange capacity of the NDF-treated reaction products. The exchange capacity is expressed as the capacity of the recovered material divided by capacity of the sample prior to NDF treatment.

responsible for the continued decrease in mass and exchange capacity with time at 90°C.

Epichlorohydrin treatment also reduced the swelling volume of SH and SBF. Unmodified SH and SBF occupied 11 mL/g in their fully hydrated Na^+-form (pH 9.1), while epichlorohydrin-treated SH and SBF occupied 7 and 6 mL/g, respectively. (Note that base addition for the epichlorohydrin reaction induces further swelling of the SBF. In order to maintain the fully hydrated state of the SBF during the full hydration reaction procedure, more water was required than the 10 : 1 ratio implied by the swelling volume of the original SBF.)

Cross-linking Optimization

The influence of epichlorohydrin amount and reaction time with SH and SBF was examined for the fully hydrated reaction procedure. A reaction time of 4–6 h was sufficient to maximally increase the stability of SH and SBF mass and ion-exchange capacity under NDF treatment conditions (Fig. 2). Increasing the amount of epichlorohydrin added to the reaction mixture from 5 to 14 mL gradually increased SH and SBF mass stability, while the exchange capacity of the NDF-treated material was largely invariant (Fig. 3). Addition of more than 14 mL of epichlorohydrin, or reaction at higher tem-

peratures, did not further improve stability (data not shown).

Epichlorohydrin cross-linking efficiency was improved greatly by reducing the amount of water added to the reaction mixture (see Experimental for minimal hydration reaction conditions). SH and SBF treated with 5 mL of epichlorohydrin under minimal hydration conditions had stabilities of mass and exchange capacity comparable to those obtained with 14 mL of epichlorohydrin under the fully hydrated regimen (compare Table III values with data for cross-linked materials in Tables I and II, and 1-day incubated samples in Fig. 1). There was no significant difference between the 3-, 4-, and 5-mL epichlorohydrin treatments (Fig. 4), indicating that even lower amounts of cross-linking reagent may be effective under reduced hydration reaction conditions. No reaction time optimization was conducted for the minimal hydration procedure. A 6-h reaction time was used for all samples, based on the results found for the fully hydrated reaction conditions (see above).

DISCUSSION

The ideal ion-exchange material should have the following characteristics: low production cost, high

O Mass Recovery   ● Ion—Exchange Capacity
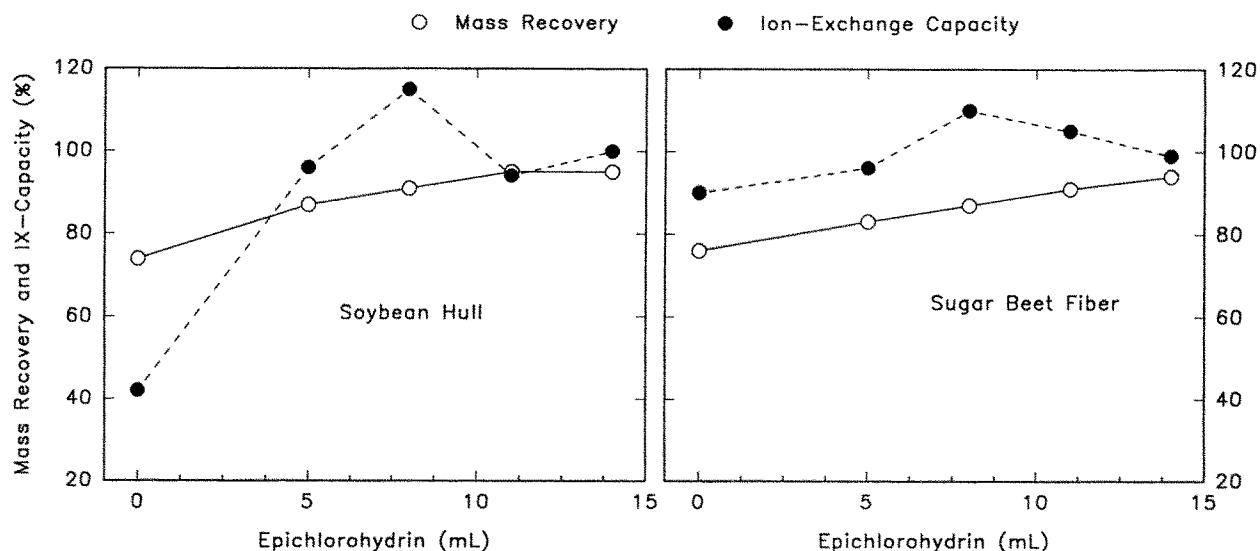
Figure 3 Effect of epichlorohydrin amount on extent of cross-linking. Soybean hull and sugar beet fiber were treated with varying amounts of epichlorohydrin for 6 h under fully hydrated reaction conditions. The zero epichlorohydrin samples were not treated with base. The effectiveness at each added epichlorohydrin amount was determined by measuring the NDF fraction (mass recovery) and exchange capacity of the NDF-treated reaction products. The exchange capacity is expressed as the capacity of the recovered material divided by capacity of the sample prior to NDF treatment.

selectivity for target ions, high durability, easy regenerability, and immunity to fouling. For most uses, synthetic resins meet these goals, except for the first and last criteria. An objective of numerous studies conducted on various agricultural by-products has been to find cost-effective alternatives to synthetic ion-exchange resins. An important requirement for such by-products is that they be widely available in order to minimize transportation costs. SH and SBF (in the form of raw pulp) satisfy this requirement

Table III Stability of Mass and Ion-Exchange Capacity of SH and SBF Cross-Linked With 5 mL of Epichlorohydrin Under Minimal Hydration Conditions

Treatment Regimen	SH Recovery (%)[a]		SBF Recovery (%)	
	Mass	Capacity	Mass	Capacity
NDF	99 ± 1	98 ± 2	97 ± 1	111 ± 9
Soxhlet	88 ± 1	80 ± 2	63 ± 6	67 ± 9
90°C/Na Borate[b]	95 ± 11	96 ± 1	86 ± 1	93 ± 6

[a] Mean and coefficient of variation.
[b] Treatment for 1 day.

since they are produced in large amounts in many geographical areas.

Many agricultural by-products have useful exchange capacity, but without some kind of chemical modification these materials do not have adequate physical stability for most applications in process water or wastewater treatment. This is true also for SH and SBF. The three tests (NDF, soxhlet, and sodium borate buffer treatment at 90°C) for physical stability gave somewhat different results when applied to unmodified materials (Tables I, II; Fig. 1). In general, the soxhlet and NDF procedures were the harshest and mildest treatments, respectively. The NDF procedure subjected the materials to a comparatively brief heat treatment. The amylase component of the NDF protocol would be expected to have little effect on either SH or SBF, as they contain negligible amounts of starch. The detergent (sodium dodecyl sulfate) component of the NDF protocol would also be expected to have very limited impact on the composition of SH and SBF because the contribution of protein to the mass and ion-exchange capacity of the materials is small (< 10%).[12,13] Thus, temperature and length of treatment time should be the predominant influences on recoverable mass and ion-exchange capacity of the residues. However, the fact that the soxhlet treatment, which was conducted at a lower temper-
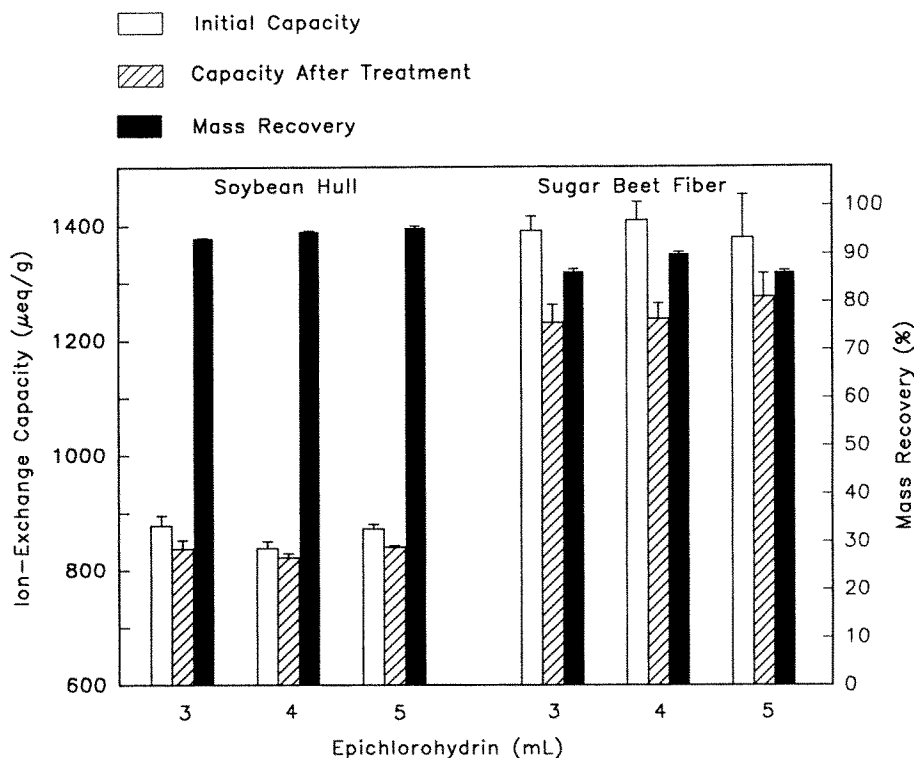
Figure 4 Cross-linking under minimal hydration conditions. Soybean hull and sugar beet fiber were treated with 3–5 mL of epichlorohydrin under the conditions detailed in Experimental for the minimal hydration reaction. Mass recovery and ion-exchange capacities are for samples treated 1 day at 90°C in sodium borate buffer.

ature than treatment with sodium borate buffer, resulted in extraction of a larger amount of material, indicates that other factors, such as pH and ionic strength, may be important. Beyond simple extraction, these test procedures might also result in thermal degradation of polymers, which could lead to losses of insoluble mass and ion-exchange capacity.[14]

Epichlorohydrin treatment greatly improved SH and SBF physical stability, and increased cation-exchange capacity as well (Tables I, II; Fig. 1). The effectiveness of epichlorohydrin in cross-linking SH and SBF polymers was anticipated because of prior reports of its use on similar materials. Isolated pectins[15] and high-pectin content cell wall substrates[5] have been shown to be readily cross-linked by epichlorohydrin. Minimizing the water content of the reaction mixture greatly increases cross-linking efficiency, presumably by lessening interpolymer distances and unproductive epichlorohydrin reactions. This is consistent with the findings of Kumari and Phalgumani[16] who reported that the vapor phase application of epichlorohydrin to cellulosic films is highly efficient. The observed cation-exchange capacity of the cross-linked SH and

SBF materials (Table I), as determined by the calcium binding assay, is consistent with the total uronic acid content reported for these materials.[11,17]

A cost comparison of the cross-linked SH and SBF materials with commercially available exchange resins demonstrates the savings potential afforded by use of agricultural residues. Carboxymethyl cellulose is a synthetic ion exchanger with properties similar to those of cross-linked SH and SBF. Carboxymethyl cellulose has an exchange capacity of about 1 meq/g, slightly above that of cross-linked SH and slightly less than cross-linked SBF. All three materials have a binding preference for multivalent cations. At current market prices,[18] carboxymethyl cellulose costs about $8.30 per equivalent of exchange capacity. The cost of SH or SBF (the raw pulp) is currently $0.11/kg. Applying epichlorohydrin ($2.20/kg) at a ratio 1 mL to 4 g of SH or SBF under the prescribed minimal hydration conditions would result in cross-linked residues costing $1.40 and $1.00 per equivalent for SH and SBF, respectively. These prices do not include production costs, only material costs. As indicated by the Figure 4 data, use of even less epichlorohydrin may give sat-

isfactory results. (Uniform dispersion of epichlorohydrin and base throughout the SH and SBF slurries is difficult under the minimal hydration conditions, a problem that might be surmountable by adroit engineering.) Obviously, cross-linked SH and SBF are far less expensive than carboxymethyl cellulose on a per equivalent basis. The least expensive synthetic cation-exchange resin in wide commercial use, sulfonated polystyrene, is approximately twice as expensive, on a per equivalent basis, than cross-linked SH and SBF.

Although cross-linked SH and SBF can be regenerated as easily as synthetic cation exchangers, it is envisioned that their most appropriate application would be as single-use prefilters to conventional ion-exchange resin beds or other water treatment technologies. In this role the agricultural residues would serve to protect and extend the service life of the primary treatment facility.

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