Cation Exchange Resins Prepared from Phytic Acid

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ABSTRACT: A novel series of water-insoluble cation-exchange resins was produced by heating a commercial phytic acid solution with any of several organic and inorganic materials possessing multiple hydroxyl functionality. Suitable materials for use as substrates were pure polysaccharides such as starch or cellulose, complex polysaccharide mixtures such as those found in agricultural residues (sugar beet pulp, corn bran, or oat hull), simple sugars such as sodium gluconate, and some polymeric inorganics such as silica and powdered glass. These materials were heated with phytic acid at 180°C for 20–35 min *in vacuo*. The brown to black material produced had an ion exchange capacity for calcium that ranged from 780–5700 μequiv/g. The silica- and glass-based resins may be suitable materials for the cleanup of radioactive wastes. They have a low carbon content (1–3%), and subsequent vitrification to stabilize the radioactive elements in an insoluble form is simplified because the matrix of the resin is silica. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 491–497, 1997

Key words: phytic acid; ion-exchange resin; corn bran; starch; cellulose

INTRODUCTION

Ion exchange resins are widely used to recover metals from industrial waste streams and to remove noxious materials from the effluents produced during food and chemical processing and in large water treatment applications. Because of variations in the character of the waste streams, one do-it-all material or method is infeasible. Resins with different selectivity properties are needed to cope with the wide variety of problems encountered. The most commonly used cation exchangers are based on sulfonated polystyrene. Alternative resins based on phosphoric acid would provide new materials with a different range of activities. Currently available phosphoric–acid-based ion exchange resins have different ion selectivity properties than sulfonic–acid-based resins[1] but are expensive. They have limited exchange capacities because the phosphoric acid groups are randomly scattered throughout the polymer matrices. Some phosphoric acid-type materials have an ability to exchange cations over a wide pH range. For example, the chelating ability of phytic acid (*myo*-inositol hexakisphosphate) extends over a broad pH range.[2] By analogy, one would expect an ion exchange resin prepared with phytic acid to exhibit these qualities also (i.e., a different selectivity spectrum than the sulfonic–acid-type resins and an effective ion-exchange capability over a broad pH range). Phytic acid has six phosphate groups associated with it (12 exchangeable hydrogens). Ideally, the attachment of one phytic acid group to a polymer hydroxyl through one of the phosphate groups (such as an ester) will establish 11 exchangeable hydrogens at that position. The actual number is somewhat less owing

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 USDA implies no approval of the product to the exclusion of others that may also be suitable.

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to competing reactions such as crosslinking and pyrophosphate formation. This circumstance affords an opportunity to produce a unique phosphoric–acid-based material with a much larger exchange capacity than those currently available. Such a substance could contain multiple regions having a high density of ionizable phosphate groups within the polymer matrix, which is unlike the randomly scattered phosphoric acid groups in the currently available resins. Consequently, a new series of resins based upon phytic acid may have properties that will complement the widely used sulfonic–acid-based cation exchangers. To this end, phytic acid was investigated as a possible starting material for the preparation of a series of cation exchange materials.

Phytic acid is a renewable resource. It is a water soluble, ubiquitous plant product readily available in large quantities that currently has few major uses. Substantial quantities of phytic acid are potentially available from cereal grains, oilseeds, and legumes. Most seeds contain 1–3% phytic acid by weight. Some meals and grain fractions can contain as much as 6.4%.[3] Several methods are available for extraction and purification of phytic acid from these sources.[4] For example, phytic acid can readily be extracted from rice bran with dilute sulfuric or hydrochloric acid and from corn steep liquor by the careful addition of calcium hydroxide. Huge amounts of rice and corn are produced yearly and could serve as convenient sources for substantial amounts of phytic acid. Both contain about 0.89% phytic acid.[5] World production of corn and rice for 1993 was estimated to be 467,925,000 and 350,369,000 metric tons, respectively.[6] Consequently, the phytic acid potentially available from these two crops alone totaled 7,282,816 metric tons. Even if only 0.1% of the total were economically recoverable, the amount available is still a respectable 7282 metric tons or 16.05 million pounds. The removal of phytic acid from grain for use in the production of an ion exchanger affords an additional advantage in that an antinutritional factor is removed from the residue.

Presently, much of the phytic acid is carried through the processing cycle and ends up in animal feed. For example, in the corn wet milling industry the majority of the phytic acid is in the steep liquor and ends up pelletized with corn bran and sold as an animal feed. Because phytic acid reduces the bioavailability of calcium and zinc, use of this material as a feed for poultry, hogs, and fish can present a nutritional problem.[7] Also, phytic acid is only partially digestible. Consequently, large amounts of phosphate end up in the feces and complicate an already difficult groundwater pollution problem. Thus, the removal of phytic acid to prepare an ion exchange resin prior to pelletizing the corn steep liquor would have the additional advantages of improving the nutritional quality of the feed by eliminating this antinutritional factor and simplifying a water pollution problem. A starch–phytate polymeric material prepared by heating a mixture of starch and a commercial phytic acid mixture has been described recently.[8] The material produced had an ion exchange capacity comparable with the commonly used sulfonic–acid-based resins, good stability towards acids, and moderate stability toward bases. This article documents the application of a similar reaction sequence to a variety of substrates whose only commonality is the presence of hydroxyl functionality. The reaction appears to have general applicability to these type compounds.

EXPERIMENTAL

Materials and Equipment

Phytic acid was obtained as a 40% (w/w) aqueous solution from Aldrich (Milwaukee, WI). Corn bran was Bestbran 90 from A.E. Staley (Decatur, IL); corn cob was from the woody part of the cob (Grit-o-cob 1420) and was supplied by The Andersons (Maumee, OH). Oat hull was an unsieved sample containing stringy particles from 0.1 to 3.3 mm in length. Soybean hull (18–40 mesh) was from Lauhoff Grain Co. (Danville, IL). Sugar beet fiber was a sugar beet pulp product that had been treated with SO_2 to reduce color formation during drying (Duofiber), produced by American Crystal Sugar Co. (Moorhead, MN). Dent starch (granule size around 15 μm) and amylomaize VII starch were from American Maize-Products Co. (Hammond, IN). Other materials included rice starch (granule size around 5 μm), cellulose powder (20 μm), chitin, paper (newsprint), paper (copier), polyvinyl alcohol (average mol wt 85-146 $\times 10^3$), powdered glass (70–200 μm), celite 545, β-cyclodextrin, and sodium gluconate. Silica powder (40 μm, Silicar CC-4 for column chromatography) was supplied by Mallinckrodt (Paris, KY). A standard-sized Kugelrohr distillation apparatus

from Aldrich (Milwaukee, WI) with temperature control (Digitherm Model TC-10, Nichols Scientific Instruments, Columbus, MO) was used for the preparation of the resins. For high-pressure liquid chromatography (HPLC) the following columns were used: Aminex HPX-87H (9-μ packing, 300 $\times$ 7.8 mm) from BioRad (Hercules, CA); Hypersil MOS-2 C-8 (5-μ packing, 250 $\times$ 4.6 mm) from Runcorn (Chesire, UK); and a PRP-1 (5-μ packing, 150 $\times$ 4.1 mm) from Hamilton Co, (Reno, NV). The HPLC detectors were as follows: Altex Model 156 refractive index detector from Beckmann Instruments (Allendale, NJ); Waters Model 410 refractive index detector (Marlborough, MA); and a SpectraPhysics (Freemont, CA) Model 8440 variable wavelength ultraviolet detector. A Perkin–Elmer Plasma 400 emission spectrometer was used to measure cations. Metal calibration standards were obtained from Spex Chemical (Metuchen, NJ).

Preparation of Ion Exchange Resin

A slurry was prepared in a 500-mL round-bottom flask by mixing 5 mL of a commercial phytic acid solution and 10–30 mL of water (or methanol) with 10 g of various substrates such as corn bran, corn cob, oat hull, soybean hull, sugar beet pulp, starch (amylomaize, dent, and rice), cellulose, paper (newsprint) and coated paper (copier paper), chitin, polyvinyl alcohol, β-cyclodextrin, sodium gluconate, powdered glass, silica, and celite. In some experiments the ratio of substrate to phytic acid solution was varied to determine the effect of this variable on the quality of the resin isolated. The water or methanol was removed on a rotary evaporator (50–70°C at 20–30 mm Hg). With some materials large clumps were formed. These were powdered in a coffee grinder before heating in the Kugelrohr. The dried residue was placed in the Kugelrohr and heated at 180° *in vacuo* (20–30 mm Hg) for 20–35 min. The brown to black material was sequentially washed with two 50-mL portions of water and methanol and then air dried. The yields of air-dried solids ranged from 4.5–11 g. Resins prepared from the various substrates had an ion exchange capacity for calcium of 780–5700 μequiv/g. Theoretically, the incorporation of one phytic acid molecule to one glucose unit in starch or cellulose would give a material with an exchange capacity of 13400 μequiv/g.

High Performance Liquid Chromatography

Phytic Acid Solutions

The mobile phase was prepared by adding 20 mL of tetrabutylammonium hydroxide and 5 mg of phytic acid to 485 mL of water. The pH was adjusted to 2.65 $\pm$ 0.05 with phosphoric acid (around 2.4 mL), and 515 mL methanol was then added. When it became cool, the buffer was filtered with the aid of vacuum through a 0.45-μm nylon filter to remove any particulates and to deaerate. The mobile phase was pumped through a heated (45°C) Hamilton PRP-1 column at 1 mL/min. Detection was by refractive index (Waters Model 410).

Distillates from Resin Preparation

A 0.01*N* sulfuric acid solution was pumped through a heated (45°C) Aminex HPX 87H column (300 $\times$ 7.8 mm) at 0.7 mL/min. Peak detection was by refractive index (Altex Model 156).

Atrazine

A 57% buffered (5.0 m*M* phosphate buffer; pH 6.8) methanol–water solution was pumped through a Hypersil C-8 column at 1 mL/min. The atrazine peak appeared at 9.8 min and was detected by ultraviolet spectroscopy at 254 nm.

Measurement of atrazine binding. Samples of resin (41 $\pm$ 1 mg) were suspended in 1-mL portions of an aqueous atrazine solution (70 μg/mL) and shaken for 60 min. The suspension was centrifuged at 14,000 rpm for 6 min, and then aliquots of the supernatant solutions were injected into the Hypersil C-8 column.

Measurement of Calcium-Binding Capacity

A sample of the resin (100–200 mg) was suspended 2 h in a stirred, buffered solution (100 mL of 2.0 m*M* MOPS, pH 7.0–7.2) containing 2.0 m*M* calcium chloride. The presence of unbound calcium ion was determined colorimetrically with tetramethylmurexide.[9]

Measurement of cation removal from aqueous solutions

A sample of the resin prepared from starch (33–56 mg, 5700 μequiv/g) was suspended in an aqueous solution (5.0 mL, pH 2.5–2.8) containing 0.01 mmol of the cation being studied (nitrate salts of

Cu^{2+}, Cr^{3+}, Ag^{1+}, La^{3+}, Fe^{3+}, Ca^{2+}, Sr^{2+}, Cd^{2+}, Pb^{2+}, Mg^{2+}, and Zn^{2+}) and agitated for 2 h on a rotator. The suspension was centrifuged at 2,500 rpm, and the supernatant solution was analyzed for unabsorbed cation. The initial and final concentrations of the cation were determined by ICP (inductively coupled plasma) atomic emission spectroscopy.

RESULTS AND DISCUSSION

Phytic Acid Solution

Pure polysaccharides such as starch, cellulose, and chitin; complex mixtures of polysaccharides such as sugar beet pulp, soy hull, corn cob, and corn bran; simple carbohydrates such as β-cyclodextrin or sodium gluconate; and complex silica-containing materials are converted into cation exchange resins by treatment with phytic acid at elevated temperatures. Commercial phytic acid solutions (40–50%) are available from several vendors. Even though these solutions contain mixtures of inositol phosphates, they are satisfactory for the preparation of the cation-exchange resins described in this article. Phytic acid solutions from the various vendors were analyzed by HPLC and found to contain as little as 22.5%, and not more than 89.1%, phytic acid and considerable amounts of other inositol phosphates. The ratios of tris- , tetrakis- , pentakis- , and hexakisinositol phosphates (IP3, IP4, IP5, and phytic acid IP6) also varied from vendor to vendor and from batch to batch. The phytic acid solution used for almost all of the experiments reported here had the following analysis: 11.2% (IP3), 20.9% (IP4), 37.2% (IP5), and 30.7% (IP6, phytic acid). These values are normalized peak areas. Typical examples of materials treated and the exchange capacities for calcium of the products formed are listed in Table I.

Variables Affecting Yields and Ion-Exchange Capacities of the Resin

Temperature

The temperature of the reaction, the time of exposure at that temperature, the pressure at which the reaction was run, the ratio of phytic acid to substrate, and the type of substrate all affected the quality of the resin produced. The effect of increasing the temperature above that suggested in the protocol was demonstrated with the starch-based resin. A 1 : 1 mixture of starch and phytic acid was heated for 20 min *in vacuo* at 180°C. The resin produced had an ion-binding capacity of 3960 μequiv/g and a mass of 10.2 g. When the temperature was raised to 200°C for 20 min, the ion-binding capacity of the resin fell 25%, and the mass fell by 18%. The resin can also be produced at lower temperatures. However, longer heating periods are required to prepare a suitable resin. For example, 2 h are needed when the temperature of the reaction is lowered to 135°C (ion exchange capacity of resin = 2810 μequiv/g).

Period of Heating and Presence or Absence of Vacuum

An unusual problem arose with the paper samples. They were initially pulped by mixing 10 g with 200 mL water and pulverizing in a Waring blender for 1 min. When the dried pulp was ground in a coffee grinder, it became cotton-like. Because of the pulp's bulk, a larger volume of water (or methanol) was used to wet the substrate completely. In this series the ratio of substrate to milliliters of phytic acid solution was 1 : 1. Heating at atmospheric pressure and for longer periods of time resulted in reduced mass and reduced resin exchange capacity. For example, when newsprint was heated under the prescribed conditions, the resin produced had an exchange capacity of 3800 μequiv/g and a mass of 14 g. The combined effect of both variables was dramatic. When no vacuum was used and the period of heating was increased to 50 min, the exchange capacity fell to 1,040 μequiv/g and the mass to 9.7 g (reductions of 72% in exchange capacity and 31% in mass). Cellulose, corn bran, and sugar beet pulp were heated with phytic acid with and without vacuum to determine the effect of this single variable on the amount of resin produced and its exchange capacity (Table II). In this series of experiments the ratio of substrate to phytic acid was 1 : 1. Heating *in vacuo* (water aspirator, 20–30 mm Hg) improved the exchange capacity of the resin by about 40% and increased the yield of resin by about 30%. A comparison with the data from the experiment with newsprint in which the duration of heating and the effect of vacuum on the resin were combined with this experiment in which the vacuum was the sole variable indicates that the major loss in yield occurs when the reaction is run at atmospheric pressure. The reduction

Table I Exchange Capacities of Resins Produced When Various Substrates Were Heated *in Vacuo* with Phytic Acid

Material Mixed with Phytic Acid	Exchange Capacity of Resin for Calcium Ion (μequiv/g)[a]	Yield of Product[c] (g)
Corn bran	2620	9.8
Corn cob	1920	10.5
Oat hull	1740	10.0
Soy hull	1720	9.6
Sugar beet pulp	2720	10.0
Starch (dent)	5500 (1 : 1)[b]	10.1
Starch (amylomaize VII)	5700 (1 : 1)[b]	10.5
Starch (rice)	4860 (1 : 1)[b]	11.6
Cellulose	3490 (5410, 1 : 1)[b]	9.0 (10.1)[b]
Chitin	2130	10.4
Paper (newsprint)	3800 (1 : 1)[b]	13.9
Paper (copier)	2620 (1 : 1)[b]	12.1
Polyvinyl alcohol	785	9.5
Powdered glass	1850	10.5
Chromatography grade silica	1800	10.6
Celite	1700	12.1
β-cyclodextrin	3540	10.5
Sodium gluconate	2540	4.5

The standard reaction conditions were ration of substrate to phytic acid 2 : 1; mixture heated *in vacuo* at 180°C for 20–30 min.
[a] Mean of three determinations.
[b] Ratio of substrate to phytic acid 1 : 1.
[c] From 10-g substrate.

in exchange capacity is markedly affected by both conditions.

Ratio of Phytic Acid to Substrate

Experiments were conducted to determine the effect of changing the ratio of phytic acid to substrate on the yield and exchange capacity of the resin produced (Table III). The substrate used with phytic acid was amylomaize VII. From the data it is apparent that there is a positive correlation between the amount and ion-exchange capacity of the resin produced and the increase in the amount of phytic acid added to a fixed amount of substrate (within limits). For example, a fourfold increase in the ratio of phytic acid to substrate results in almost a fourfold increase in the ion-exchange capacity (from 1270 to 5000 μequiv/g). However, the increase in mass, although substantial, is not as dramatic (from 6.4 to 10.5 g). In-

Table II The Effect of Heating in Vacuum on the Quality of the Resin

	With Vacuum		Without Vacuum	
Substrate	(μequiv/g)	Grams of resin	(μequiv/g)	Grams of resin
Cellulose	3490	10.1	2160	7.2
Corn bran	2620	9.8	1500	7.1
Sugar beet pulp	2720	10.0	1560	7.4

The standard reaction conditions were ratio of substrate to phytic acid 2 : 1, mixture heated with or without vacuum at 180°C for 20–30 min.

Table III Effect of Reactant Ratio on the Ion-Exchange Capacity and Yield of Resin

Ratio of Phytic Acid to Amylomaize[a]	Exchange Capacity of Resin (μequiv/g)	Yield of Resin (g)
2.5	1270	6.4
5.0	2620	9.2
7.5	4290	9.6
10	5000	10.5
20	5780	10.5

The mixture was heated *in vacuo* at 180°C for 25 min.
[a] Milliliters of phytic acid solution added to 10 g of amylomaize VII.

creasing the ratio of phytic acid to substrate to 2 : 1 marginally increases the ion-exchange capacity and has no effect on the amount of resin produced. However, lengthening the reaction time from 25 to 35 min increases both quantities.

Effect of Substance Type

From Table I it is apparent that under the same reaction conditions different substrates produce products that differ in their ion-exchange capacities and in their yield. The monosaccharide sodium gluconate and the oligosaccharide β-cyclodextrin were treated as described in the protocol. They were converted to 4.5 and 10.4 g of resin, respectively. The products produced from sodium gluconate and β-cyclodextrin were insoluble in water and had an exchange capacity of 2540 and 3540 μequiv/g, respectively. Polymerization and crosslinking have obviously occurred with these substrates. In this series of experiments the resins produced from the silica-based materials appear to top out with an ion-exchange capacity of around 1800 μequiv/g (i.e., doubling the ratio of phytic acid to substrate did not significantly increase the yield or exchange capacity of the resin). However, by modifying the reaction conditions (heating time, temperature, and suspending solvent) the exchange capacities of the glass- and silica-based resins can be raised to 2600 and 4100 μequiv/g, respectively. These silica-based resins may offer some unique advantages in the removal of radioactive wastes from the environment. They not only remove the radioactive elements from acidic solutions by ion exchange, but the predominantly silica-based (only 1–3% carbon) resin can serve as a matrix for vitrifying the bound radioactive elements. Use of borosilicate glass may offer the added advantage of moderating neutron flux. Although, the agricultural residues show significant increases in exchange capacity and yield when the ratio of phytic acid to substrate is increased, the increases are not as large as the increases shown with starch and cellulose.

The volatile degradation products that result during the production of the resin at 180°C were collected in an ice trap and analyzed by HPLC. A typical example was the distillate from the starch–phytic acid resin. The chromatogram had 16 peaks. Of these, 7 were readily identified by comparing their retention times to those of authentic samples. The identified peaks and their retention times in minutes are as follows: levoglucosan (11.40), formic acid (12.8), acetic acid (13.9), levulinic acid (15.3), crotonic acid (25.1), hydroxymethyl furfural (32.4), and furfural (47.7). These peaks represent 82% of the total normalized peak area. As expected, the resins prepared from the other agricultural residues gave distillates that had many common components but differed in the their ratios. These differences are a reflection of their dissimilar polysaccharide content. A typical example is the distillate produced from sugar beet pulp: the ratio of acetate to the other components was four times greater than that found in starch. Only minimal amounts of distillate were formed during the preparation of the silica, glass, and celite resins.

Removal of Cations and Atrazine from Solution

The selectivity of the starch–phytate ion-exchange resin for different metal ions in an acidic (pH 2.5–2.8) solution was evaluated (Table IV).

Table IV Efficiency of Cation Removal from Aqueous Solutions by Starch–Phytate Resin

Cation in Solution	Remaining After Treatment (%)
Cu^{2+}	2.0
Cr^{3+}	1.1
Ag^{1+}	29.9
La^{3+}	5.7
Fe^{3+}	40.6
Ca^{2+}	9.5
Cd^{2+}	3.2
Pb^{2+}	1.5
Mg^{2+}	9.1
Zn^{2+}	8.1
Sr^{2+}	4.8

Equimolar amounts of the various cations were mixed with the starch-based resin (33–56 mg). The concentration of cation before and after the addition of the resin was measured, and the difference was deemed to reflect the ability of the resin to remove that particular cation from solution. After adjustment for the variable amount of resin added, the percentage of the cation removed was considered to be a rough estimate of the relative selectivity of the resin for the various cations: Cr > Pb > Cu > Cd > Sr > La > Zn > Mg > Ca ≫ Ag > Fe. The order of selectivity is somewhat different than that found with the typical sulfonated styrene–divinylbenzene resin (Ag > Pb > Sr > Ca > Cd > Cu > Zn > Mg).[10] Atrazine was readily removed (more than 95%) from aqueous solutions by all of the carbon-based products. In contrast, the starting substrate and the silica-based products removed less than 5%. Apparently, some adsorption phenomenon occurs between atrazine and the partially pyrolyzed carbon-based products. These products can thus serve a dual role: an ion-exchanger and an adsorption material.

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