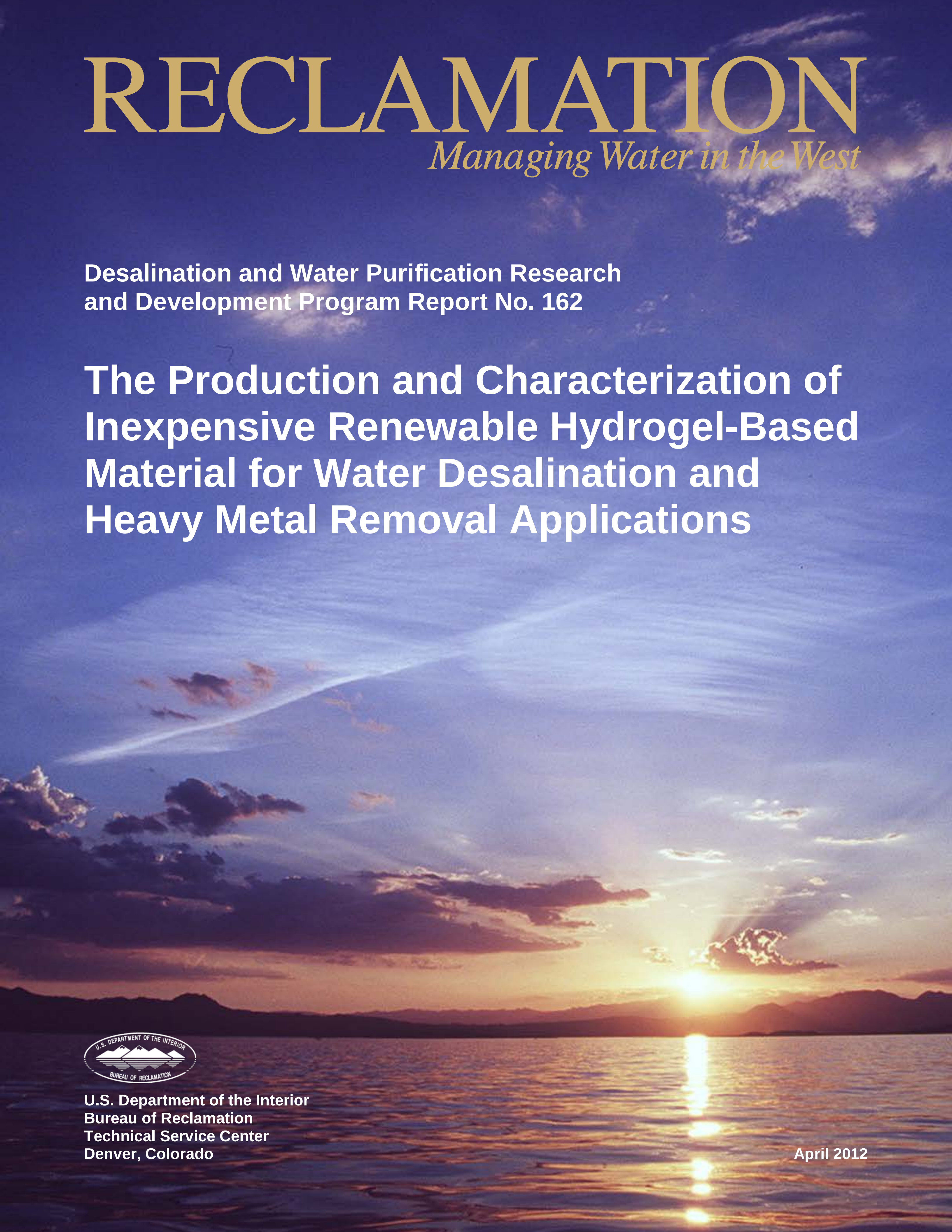

RECLAMATION

Managing Water in the West

Desalination and Water Purification Research
and Development Program Report No. 162

The Production and Characterization of Inexpensive Renewable Hydrogel-Based Material for Water Desalination and Heavy Metal Removal Applications

U.S. Department of the Interior
Bureau of Reclamation
Technical Service Center
Denver, Colorado

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14. ABSTRACT

The research conducted for this project was organized around seven major tasks: (1) Optimize material composition to produce highly effective hydrogels; (2) Define effective, inexpensive routes to produce high-performance hemicellulose citrate-chitosan hydrogel particles with various composition and structure; (3) Characterize the desalination of water using these hydrogel particles; (4) Characterize the heavy-metal uptake of water using these hydrogel particles; (5) Evaluate the regeneration of these materials, making the process even less expensive; (6) Develop effective continuous processes for applying these materials; (7) Summarize the economic viability of these processes and indicate technologies in which they surpass existing technologies both for economic and other reasons.

This report describes research accomplishments and provides additional pertinent information relevant to each of these tasks.

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Hydrogel, water desalination, heavy-metal removal, hemicellulose, chitosan

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Prepared for the Bureau of Reclamation Under Agreement No. R10SF80251

by

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U.S. Department of the Interior
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MISSION STATEMENTS

The U.S. Department of the Interior protects America's natural resources and heritage, honors our cultures and tribal communities, and supplies the energy to power our future.

The mission of the Bureau of Reclamation is to manage, develop, and protect water and related resources in an environmentally and economically sound manner in the interest of the American public.

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ACRONYMS AND ABBREVIATIONS

DD	degree of deacetylation
DI	deionized
ES	equilibrium swelling
FTIR	Fourier transform infrared spectroscopy
HCCC	hemicellulose citrate chitosan
kWh	kilowatt-hour
mEq	milli-equivalent
MW	molecular weight
TGA	thermogravimetric analysis

METRIC CONVERSIONS

The metric equivalents for non-metric units used in the text are as follows:

Unit	Metric equivalent
1 gallon	3.79 liters
1 kilowatt-hour	3.6 megajoules
1 pound (lb)	0.45 kilograms
1 ton	907 kilograms

INTRODUCTION

The research conducted for this project was organized around seven major tasks:

Task 1: Optimize material composition to produce highly effective hydrogels. This task included studying both the effect of the hemicellulose source and the effect of chitosan deacetylation.

Task 2: Define effective, inexpensive routes to produce high-performance hemicellulose citrate-chitosan hydrogel particles with various composition and structure.

Task 3: Characterize the desalination of water using these hydrogel particles.

Task 4: Characterize the heavy-metal uptake of water using these hydrogel particles.

Task 5: Evaluate the regeneration of these materials, making the process even less expensive.

Task 6: Develop effective continuous processes for applying these materials. This task included both constructing a fluidized bed system and testing various materials in the system.

Task 7: Summarize the economic viability of these processes and indicate technologies in which they surpass existing technologies both for economic and other reasons.

REPORT ON TASK 1

Task 1: Optimize Material Composition to Produce Highly Effective Hydrogels

During this project we have characterized the hemicellulose derived from birch wood, mixed hardwood, and switchgrass for use in this technology. We have also produced a series of chitosans with varying levels of deacetylation. This material was created from chitin and in conjunction with hemicellulose produced stable foams. The chitosan that was produced was directly compared with commercially purchased chitosan. In the lab, we used a mild form of deacetylation, and the net result was a high molecular chitosan when compared to the commercially purchased sample. The range of the deacetylation was from about 82 up to 100 percent. A deacetylation of ~80 percent is required for the chitosan to become soluble. We also created cross-linked hemicellulose-citrate chitosan foams and measured the performance of these materials with respect to heavy-metal uptake (lead, cadmium, selenium, arsenic). The results are summarized below.

A. Extraction of Hemicellulose from Different Types of Woody and Non-Woody Plants

The extraction of hemicellulose from raw materials is carried out in a two-step process. The experimental details are discussed here. The first step involves extracting the holocellulose, from which the hemicellulose is isolated. To accomplish this, one first must weigh out accurately, 5.0 g of oven-dried finely ground plant material and transfer it to a 500-mL Erlenmeyer flask. Next, add 200 mL of water, 2.5 mL of glacial acetic acid, and 7.5 g of sodium chlorite to the ground plant material. Then, cover the 500-mL flask and place it in the oil bath at 80 °C for one hour. Every 30 minutes for three applications, add 2.5 mL of glacial acetic acid and 7.5 g of sodium chlorite for a total of four identical treatments. At the completion of the fourth addition, recover the holocellulose by filtration, wash with distilled water several times, and then dry in an oven at 70 °C.

To extract the hemicellulose from the holocellulose, into a 1,000-mL conical flask, weigh accurately the equivalent of 5.0 g of oven-dried holocellulose. Add 250 mL of 18-percent aqueous sodium hydroxide solution. Seal the flask with a rubber stopper, shake the mixture for 1 hour, and then let the mixture stand at room temperature for 30 minutes. Next, filter the solution on filter paper to separate the α-cellulose. After separation of the α-cellulose, neutralize the filtrate with acetic acid and then add 250 mL isopropyl alcohol and let the mixture stand for 2 hours to precipitate the hemicellulose. After precipitation, extract the hemicellulose by centrifuging and filtering. Wash the hemicellulose precipitate with water and ethanol several times, and then dry it in an oven at 70 °C.

i. Results and Discussion of Hemicellulose Isolation

The extractions of hemicellulose from various types of plant material are reported in Table 1. The percent yield of hemicellulose from birch wood was significantly higher than the yield from other plant materials examined. The hardwoods, as expected, exhibited a greater yield in hemicellulose when compared to the softwoods. The yield of hemicellulose from switchgrass (non-woody material) was higher than the yield from softwood and close to that of hardwood. A trend similar to that observed for the yield was found for the molecular weight, with the hardwoods having higher molecular weight than softwoods and the switchgrass being similar to the hardwoods.

Table 1. Extraction of Hemicellulose from Various Types of Wood and Its Molecular Weight

Wood Species	Yield of Holocellulose (%)	% of Extracted Hemicellulose		Molecular weight (g/mol)
		Based on Wood	Based on Holocellulose	
Birch	73.90	14.18	19.20	60,540
Eucalyptus	74.40	9.23	12.40	54,925
Commercial mix of hardwood	62.60	8.78	14.03	55,916
Spine	63.58	6.74	10.60	48,126
Spruce	58.30	3.45	5.92	49,786
Commercial mix softwood	59.10	4.62	7.83	48,826
Switchgrass	54.23	7.95	14.66	55,982

The sugar composition for the birch wood indicates that the extracted hemicellulose is not solely xylan. The content of glucose, arabinose, and mannose is actually much higher than the xylose content, indicating the presence of multiple types of hemicellulose. The mixed hardwood showed no xylose, indicating a very low presence of xylan. The switchgrass had an overall composition similar to that of the birch wood, but had less arabinose and mannose. This finding may indicate that good quality hemicellulose can be isolated from switchgrass. (See Table 2).

B. Deacetylation of Chitin to Produce Chitosan

Chitin samples (1 g each) were stirred in NaOH (20 mL, 50 wt %) in flasks. The flasks were heated in an oven to 100 °C for periods of 1, 4, 8, 12, or 16 hours. After heating, each reaction mixture was cooled to room temperature, filtered and neutralized by washing with deionized water 20 times and then again washed with ethanol (1:50). After washing, the deacetylated chitin was filtered and washed with deionized water two times and dried at 80 °C overnight in an oven. The reaction is depicted in Figure 1. Deacetylated chitin and some other samples are shown in Figure 2.

Table 2. Total Amount of Sugar in Various Types of Bleached Wood Before and After Extraction

Sample	Sugars (g/100g), Pre-Extraction[1]				Extracted hemi-cellulose (g/100 g wood)	Sugars (g/100g), Post-Extraction[2]			
	Glucose	Xylose	Arab+ Manose	Total		Glucose	Xylose	Arab+ Manose	Total
Birch wood	6.28	2.54	5.10	13.92	18.65	7.21	2.02	5.78	15.01
Mixed hardwood	5.20	- - -	2.3	7.50	14.03	8.21	- - -	5.91	14.12
Switch-grass	6.48	0.85	0.38	7.72	14.66	8.61	7.28	1.06	16.95

[1] Galactose was not detected in any sample.

[2] Following extraction with isopropyl alcohol at a 1:1 ratio of liquor to solvent.

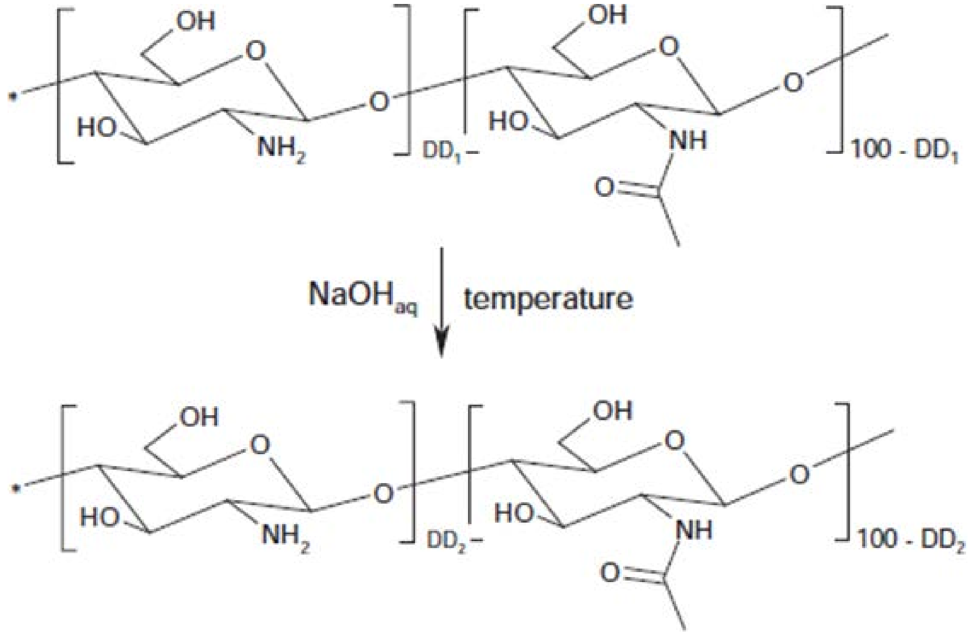
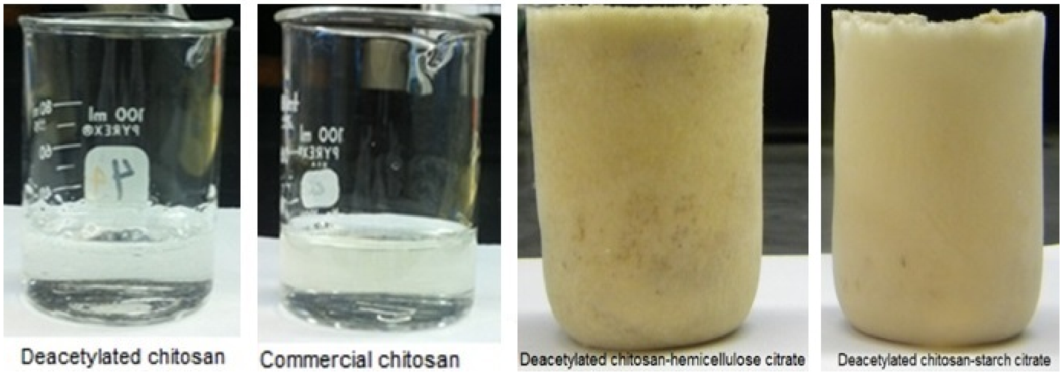


Figure 1. Deacetylation of chitin to chitosan in $NaOH_{aq}$.

(DD = degree of deacetylation. $DD_1 < 75\%$ and $DD_1 < DD_2$.)

Deacetylated chitosan

Commercial chitosan



Deacetylated chitosan

Commercial chitosan

Deacetylated chitosan-hemicellulose citrate

Deacetylated chitosan-starch citrate

Figure 2. From left to right and top to bottom: deacetylated chitosan, commercial chitosan, deacetylated chitosan solution, commercial chitosan solution, deacetylated chitosan-hemicellulose citrate foam and deacetylated chitosan-starch citrate foam.

i. Characterization of Deacetylated Chitin (Chitosan)

Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a NEXUS 670 FTIR spectrophotometer using a KBr disc containing 10 percent of finely ground sample. All the spectra were obtained by the accumulation of 256 scans, with resolution of 4 cm^{-1} over 400–4,000 cm^{-1}. FTIR absorption band ratios for determining the percent acetylation of chitosan were recorded and used to follow the rate of alkaline deacetylation of chitin. The following equation was used to determine the acetylation:

$$\%\ N\text{-acetylation} = (A_{1655}/A_{3450}) \times 115$$

where A_{1655} is the absorbance at 1,655 cm^{-1} and A_{3450} is the absorbance at 3,450 cm^{-1}.

Acid-Base Titration

Chitosan (0.1 g) was dissolved in hydrochloric acid (10 mL, 0.1 *N*). The viscous solution was diluted with water (25 mL), and four drops of a methyl orange solution (0.05 g in 100 mL) were added. The sample was titrated to color change (from red to yellow-orange) with a caustic soda solution (0.1 *N*). Additionally, for better control of the point of color change, and hence comparability, a pH meter was used to record the endpoint (pH 3.2–3.25). The calculation of the degree of deacetylation (DD) is shown in following equations:

$$DD = \frac{x}{x + \frac{m_{\mathrm{crs}}}{203}} 100$$

$$x = \frac{V_{\mathrm{HCl}}\, c_{\mathrm{HCl}} - V_{\mathrm{NaOH}}\, c_{\mathrm{NaOH}}}{161}$$

where m_{crs} is the mass of the sample, V_{HCl} and V_{NaOH} are the volumes of HCl and NaOH solution, respectively, and C_{HCl} and C_{NaOH} are the concentrations of HCl and NaOH solutions, respectively.

Molecular Weight Measurement of Chitosan

Viscometric measurements were carried out with an Ubbelohde Viscometer in 1-percent acetic acid and 0.5 *M* sodium acetate buffer at 25 °C. The molecular weight was determined to follow the Mark-Houwink equation:

$$\eta = K\,(\mathrm{MW})^{a}$$

where *K* and *a* are reference constants and MW is the molecular weight of the dilute polymer solution.

Chitin samples, immersed in a 50-wt.% NaOH solution at a solid-to-liquor ratio of 1:20, were studied after various lengths of heating at 100 °C. The degree of deacetylation of chitin was determined with two methods: titration and FTIR (Table 3, Figure 3). Both analysis methods show a similar percent of deacetylation and that the deacetylation slightly increased up to 8 hours (Table 3). While very different in approach, the two analysis methods showed excellent agreement. Chitin and chitosan are macromolecules that differ in their content of acetyl groups. The molecular weight and degree of deacetylation (DD) are responsible for the solubility of each polymer. Higher molecular weights and low amounts of deacetylation make polymers less soluble.

Typically, chitin having a DD of less than 75 percent is not soluble in an acetic medium, but chitin with a DD above 75 percent is soluble. The 1-hour deacetylated chitin was not found to be soluble in an acidic medium and thus the viscosity and MW could not be determined. After 4 hours of deacetylation, the viscosity and MW could be determined. There was a slight increase in the MW after 8 hours of treatment and then a decrease in the MW with further treatment. This could be attributed to acid hydrolysis of the chitin at longer treatment times.

Table 3. Influence of Reaction Time on the DD and MW of Chitin in NaOH
(Concentration 50 wt % NaOH, solid-to-liquor ratio 1:20, temperature 100 °C)

Sample	Deacetylation Time (hours)	Degree of Deacetylation (%)		Solubility (%) with 1% acetic acid	Viscosity (cps)	Molecular Weight (MW)
		Titration	FTIR			
Commercial chitin	0	30.10	32.50	0	- - -	- - -
Deacetylated chitin	1	72.20	72.26	0	- - -	- - -
Deacetylated chitin	4	82.40	83.95	100	1,093	2.2×10^6
Deacetylated chitin	8	84.50	86.45	100	1,198	2.5×10^6
Deacetylated chitin	12	85.00	86.25	100	390	3.8×10^5
Deacetylated chitin	16	85.81	85.00	100	317	2.7×10^5
Commercial chitosan	Unknown	83.81	84.10	100	218	1.4×10^5

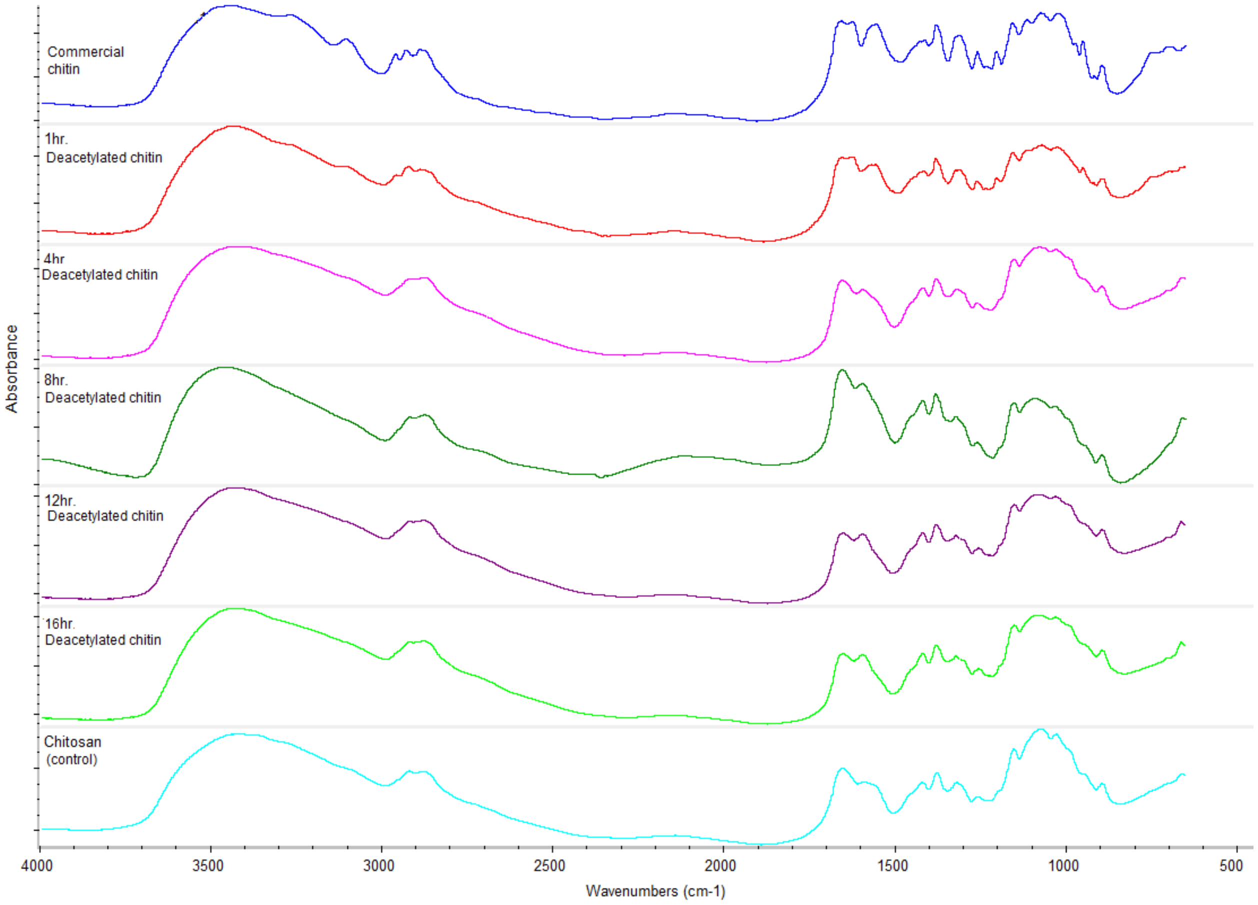


Figure 3. FTIR spectra of deacetylation of chitin to chitosan at different times.
(Concentration 50 wt % NaOH, solid-to-liquor ratio 1:20, and temperature 100 °C.)

In addition, in another experiment in which chitin was deacetylated to chitosan in a bomb digester (reaction temperature 160 °C, reaction time 5 hours, concentration 50 wt. % NaOH, and solid-to-liquor ratio 1:20) an analysis indicated that the chitin had been fully (100%) deacetylated but that it also had a significantly decreased viscosity and molecular weight (146 g/mol). It was not possible to make foam with hemicellulose citrate when the chitin was degraded to this extent. In contrast, the high-molecular-weight deacetylated chitin (chitosan) produced a more flexible and durable foam with hemicellulose citrate or starch citrate than that of low-molecular-weight commercial chitosan.

ii. Foam Preparation of Hemicellulose Citrate and Chitosan

A chitosan solution of 1 g of chitosan in 99 mL of water and 1 mL of glacial acetic acid was added to a 100-mL solution of 1% hemicellulose citrate in a 500-mL round-bottom flask, the pH was adjusted to 3.5 with sodium acetate, and the solution was stirred at 100 °C for 3 hours. The product was cooled to ambient temperature (about 1 hour) and then freeze-dried. In some cases, wood fibers, at a 1:1 ratio of fibers to hemicellulose citrate-chitosan, were blended into the reaction mixture after the reaction.

iii. Salt Uptake Experiments

Two different methods were used to determine salt uptake, such as gravimetric, conductivity, and thermogravimetric analysis. Samples of ~0.025 g were weighed and placed in a pre-weighed tea bag. The sample and tea bag were then soaked for 20 minutes in 25 mL of 3.5-percent NaCl solution. The equilibrium saline absorption was determined by allowing the tea bag to drip dry and then weighing the tea bag plus the sample. The weight of a saturated tea bag was then subtracted to determine the amount of saline taken up by the foam. The foam was then dried overnight at 105 °C, and the weight gain in the sample was taken to be the salt uptake. Salt uptakes of 1.12 g/g and 1.25 g/g were determined for the deacetylated chitin-hemicellulose citrate foam and deacetylated chitin-hemicellulose citrate/pulp foam, respectively. Conductivity tests of the initial and final solutions after exposure to the two foams indicated that the deacetylated chitin-hemicellulose citrate foam and the deacetylated chitin-hemicellulose citrate/pulp foam contained, respectively, 0.96 g/g and 1.02 g/g of NaCl not found in the control samples. To confirm, the samples were tested by thermogravimetric analysis (TGA) to 600 °C. The salt content of the sample was determined by subtracting a control residual char from the residual char weight of the sample plus the salt. The salt contents, according to this method, were found to be 1.34 g/g and 1.08 g/g salts, respectively, for the deacetylated chitin-hemicellulose citrate foam and the deacetylated chitin-hemicellulose citrate/pulp foam (Table 4 and Figure 4). Table 4 also shows the equilibrium saline absorption for the various samples. The deacetylated chitin-hemicellulose citrate/pulp foam absorbed more saline solution than the deacetylated chitin-hemicellulose citrate (no pulp) foam. The chitosan made in our laboratory was found to absorb more saline solution and to take up salt better than the commercially available chitosan.

This may be attributed to the higher molecular weight of the laboratory-prepared chitosan.

Table 4. Saline and Salts Uptake of Deacetylated Chitosan-Hemicellulose Citrate Foam

Hydrogel (Absorbent)	Equilibrium Saline Solution Absorption (g solution/g foam) (3.5% NaCl solution)	Salt Uptake (g NaCl/g foam) (3.5% NaCl solution) (TGA exposed)
Chitosan-hemicellulose citrate (control)	33.76	0.79
Chitosan-starch citrate foam (control)	32.60	0.75
Deacetylated chitin-hemicellulose citrate foam	37.80	1.34
Deacetylated chitin–starch citrate foam	33.00	0.86
Deacetylated chitin–hemicellulose citrate/pulp foam	43.92	1.08
Deacetylated chitin–starch citrate/pulp foam	38.90	0.78

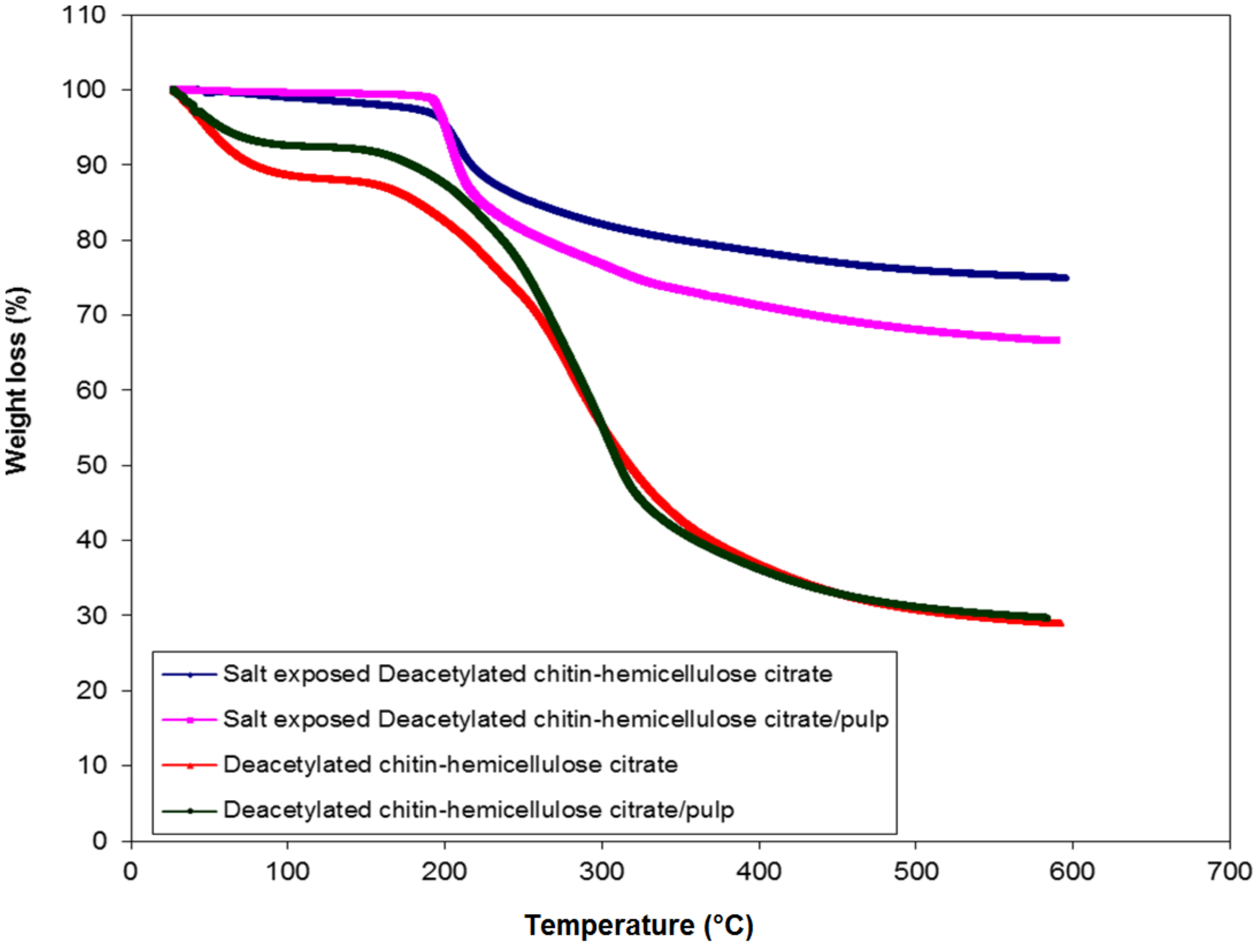


Figure 4. TGA of salt-exposed deacetylated chitin-hemicellulose citrate foam and deacetylated chitin-hemicellulose citrate/pulp foam.

Increases in weight at 600 °C indicate the pickup of inorganic salts.

C. Synthesis of Hemicellulose Derivatives with Citric Acid

Citric acid (5 g) was dissolved in a minimal amount of water (6 mL) in a glass beaker. Hemicellulose (5 g) was combined with the citric acid solution in a 100-mL glass beaker and manually mixed vigorously with a glass rod. The mixture was placed in a forced-air oven to dehydrate at 100 °C for 30 minutes. At this point, all surface moisture was removed and the hemicellulose particles were coated with citric acid. The mixtures were allowed to react in the oven under pre-determined conditions. The reaction conditions were 5 hours at 115 °C. Reaction products were slurried in water (60 mL) for 30 minutes, adjusted to pH 2 using acetic acid, filtered on filter paper, and washed with water (100 mL). The product was air dried overnight and the filtrate was evaporated to obtain a weight for yield determination.

i. Characterization of Hemicellulose Derivatives

Determination of Molecular Weight

The intrinsic viscosity of hemicellulose and hemicellulose derivatives was determined at 25 °C with an Ubbelohde-type viscometer for the measurement of molecular weight. Hemicellulose and hemicellulose citrate were dissolved with 0.04-*M* cupriethylenediamine (CED). Then 7.2 mL of the solution was added to a viscometer (No. 50) by pipette. Suction was then applied to force the solution into the bulb about 2 cm above the capillary tube. The vacuum was removed and the solution was allowed to flow down through the capillary by the force of gravity. The time it took for the solution to flow through the capillary was then recorded as the efflux time.

$$\text{Intrinsic viscosity } [\eta] = \text{time (s)} \times \text{viscosity meter constant}$$

The Staudinger-Mark-Houwink equation of the hemicellulose (xylan) solution in cupriethylenediamine is,

$$[\eta] = 2.2\times10^{-2}\, P_n^{-0.72} \tag{1}$$

here P_n = Degree of polymerization.

Total molecular weight =
Degree of polymerization × Molecular weight of monomer unit

Determination of Carboxyl Content

Using an acid-base titration, a known amount of synthesized product dissolved in excess 0.1-*N* NaOH (pH 12.5) was allowed to react with the sample as an ester for one hour. The remaining excess amount of NaOH was determined by titration with 0.1-*N* HCl using phenolphthalein as an indicator and the carboxyl content in milliequivalents of acidity per 100 grams calculated as:

$$\text{Carboxyl content} = \frac{(V_b - V_a \times N \times 100}{W}$$

where N = normality of HCl, Eq/liter

V_b = volume of HCl without sample, mL

V_a = volume of HCl in presence of sample, mL

W = weight of sample, grams

Cross-Linking Reaction between Hemicellulose Citrate and Chitosan

A chitosan solution was prepared by adding 1 g of chitosan to a mixture of 99 mL of water and 1 mL of glacial acetic acid. The chitosan solution was added to 100 mL of 1-percent hemicelluloses citrate solution in a 500-mL round-bottom flask. The pH was then adjusted to 3.5 with sodium acetate. The reaction mixture was stirred using a magnetic stirrer at 100 °C for 3 hours, followed by ambient cooling to room temperature (approximately 1 hour) and then the product was freeze-dried.

Equilibrium Swelling (ES) Method of Water Uptake

The equilibrium swelling was determined by a gravimetric method. A pre-weighed wet tea bag of size 200×100 mm was used to hold the sample. The sample was immersed into water in a Petri dish at room temperature for a predetermined time, either 0.5, 1, or 48 hours, and then poured into the pre-weighed wet tea bag. The excess water was allowed to drip off the sample by gravity. The weight of the tea bag and sample was then measured (X_a), and the equilibrium swelling (ES) was calculated according to the following formula:

$$ES = \frac{X_a - Y_b - Z_p}{Z_p}$$

where Y_b = weight of wet tea-bag

Z_p = weight of dry sample

Absorption and weight loss with an aqueous NaCl solution (concentration: 3.5%) was investigated similarly.

Vacuum Filtration Method of Water Uptake

Approximately 0.1 g of each sample was weighed and placed in a glass Petri dish. The sample was soaked in 50 mL distilled water for a predetermined time, either 0.5, 1, or 48 hours. A dry Whatman #4 quantitative filter paper circle was placed into a Buchner funnel attached to a house vacuum. The contents of the dish were poured onto the filter paper. The dish was rinsed with about 15 mL of additional deionized (DI) water, and this water was also poured into the funnel. Once the water was removed, the sample was lifted off the filter paper and then weighed to determine water absorption per gram of sample. Absorption and weight loss with an aqueous NaCl solution (concentration: 3.5%) was investigated similarly.

ii. Extracted Hemicellulose (Xylan) Reaction Results

The reaction yield, carboxyl content, and molecular weight for the different hemicelluloses is shown in Table 5. The percent yield of the extracted birch wood hemicellulose was significantly higher than the percent yield from the commercial birch wood xylan. The percent yields of mixed hardwood hemicellulose, mixed softwood hemicellulose, pine hemicellulose, and switchgrass hemicellulose were also higher than that of commercial birch wood hemicellulose. Only the spruce provided a lower yield than the commercial material.

Table 5. Extracted Hemicellulose (Xylan) Reaction Results

Sample Type	Original Sample		Post-Reaction[1]		
	Carboxyl Content (mEq/100 g)	Molecular Weight (g/mol)	Yield (%)	Carboxyl Content (mEq/100 g)	Molecular Weight (g/mol)
Commercial xylan from birch wood	324	52,600	40.00	722	42,000
Hemicellulose from birch wood	103	60,540	64.19	574	49,465
Hemicellulose from eucalyptus	55	54,925	40.10	500	47,935
Hemicellulose from commercial mixed hardwood	44	55,916	51.00	318	47,113
Hemicellulose from pine	22	48,126	44.66	123	46,671
Hemicellulose from spruce	65	49,786	38.75	292	44,917
Hemicellulose from commercial mixed softwood	24	48,826	48.75	107	44,233
Hemicellulose from switchgrass	73	55,982	42.00	524	46,105

[1] Following reaction with a citric acid crosslinking agent and a sodium hypophosphite catalyst.

The carboxyl content was increased from 324 mEq/100 g to a maximum of 722 mEq/100 g for commercial birch wood xylan, but for extracted birch wood hemicellulose, the increase was from 103 to 574 mEq/100 g. The carboxyl content was also increased to a similar level for switchgrass and eucalyptus hemicellulose (Table 5).

The intrinsic viscosities of hemicellulose and hemicellulose citrate were determined at 25 °C with an Ubbelohde-type viscometer (Table 5). Based on these measurements, the viscosity molecular weights of extracted birch wood hemicellulose and extracted switchgrass hemicellulose were higher than the molecular weight of commercial birch wood xylan. It is also observed that the molecular weight of the hemicellulose xylan citrate was 19 percent lower (for all extracted hemicellulose citrate and commercial xylan citrate) than that of the hemicellulose after reacting with citric acid at 115 °C for 5 h. This indicates that some degradation of the hemicellulose accompanied the functionalizing of the material.

In addition, based on yield, carboxyl content, molecular weight, and availability of raw material, we have decided to use birch wood xylan citrate, mixed hardwood xylan citrate, and switchgrass xylan citrate for further reaction with chitosan.

A summary of results of extracted hemicellulose citrate-chitosan foam relative to control materials (commercial xylan citrate-chitosan foam) is shown in Table 6. The water absorption with deionized water and NaCl solution was close to that of the commercial hemicellulose citrate-chitosan foam. The extracted mixed hardwood hemicellulose citrate-chitosan foam and the switchgrass xylan citrate-chitosan foam with deionized water and saline had significantly higher weight loss than the extracted birch wood hemicellulose citrate-chitosan foam and the commercial birch wood xylan citrate-chitosan foam.

Table 6. Effect of Water and Saline Absorption with Hemicellulose Citrate-Chitosan Foam

Sample	**Water Absorption (g/g)**		**Saline (3.5% NaCl) Absorption (g/g)**		**Weight Loss (%)**	
	Equilibrium Swellability	**Vacuum Filtration**	**Equilibrium Swellability**	**Vacuum Filtration**	**Water**	**Saline**
Hemicellulose citrate-chitosan foam (birch wood hemicellulose)	27.10	6.10	34.20	7.46	9.85	–6.0
Hemicellulose citrate-chitosan foam (mixed hardwood hemicellulose)	26.75	5.34	27.80	5.90	21.27	10.41
Hemicellulose citrate-chitosan foam (switchgrass hemicellulose)	27.50	6.25	34.08	7.06	17.25	–2.0
Xylan citrate-chitosan foam (commercial birch wood xylan)	31.00	7.00	36.00	8.20	8.10	–5.5

iii. Characterization of Metal Uptake

Completely mixed batch reactors were used to determine metal uptake. Deionized water was used. Arsenic, mercury, cadmium, lead, and selenium solutions were evaluated individually. Polyethylene vials were prepared with 0.025 g carbohydrate citrate-chitosan foam and 50 mL of standard metal solutions. The pH of the metal solutions was 5.1. The vials were agitated by hand for 6 minutes and then filtered through filter paper (Whatman 4) with house vacuum. Two drops of 2-percent nitric acid were added to the approximately 50 mL of filtrate. The heavy-metal concentrations of the filtrate were measured by inductively coupled plasma optical emission spectrometry.

Heavy-Metal Results

The arsenic, lead, cadmium, and selenium uptake was investigated for the birch wood hemicellulose citrate-chitosan foam, the mixed hardwood hemicellulose citrate-chitosan foam, and the switchgrass xylan citrate-chitosan foam (Tables 7–10). The arsenic and selenium absorption was significantly higher for the birch wood hemicellulose citrate-chitosan foam than for the mixed hardwood hemicellulose citrate-chitosan or for the switchgrass hemicellulose citrate-chitosan foam. It is also observed from Table 7 that the arsenic absorption with five different types of commercial metal chelating was significantly lower than it was in our experimental samples. Most of the commercial metal chelating agents are polymer resins with sulfur-active sites that may have very good binding affinity with some metals. Our experimental materials contain amine and carboxylic groups. These functional groups are similar to those found in EDTA and DTPA and are considered responsible for the metal chelating capabilities in these materials. (See Figure 5.) The advantage of our materials over EDTA and DTPA is that our materials are insoluble swollen gels that can act as sorbents in liquid.

Table 7. Arsenic Uptake for Various Experimental Materials
(Absorbent 0.025 g, 50 mL solution, and 6 minutes time)

Sample	Initial Concentration (mg/L)	Final Concentration (mg/L)	Arsenic (As) Loading (mg/g)
Birch wood hemicellulose citrate-chitosan foam	5.22	4.22	1.98
Mixed hardwood hemicellulose citrate-chitosan foam	5.22	4.92	0.58
Switchgrass hemicellulose citrate-chitosan foam	5.22	4.86	0.70
Commercial Sorba Tech 450	5.22	5.17	0.08
Commercial LaneRT	5.22	5.02	0.40
Commercial Alumina	5.22	4.98	0.48
Commercial PuroliteFerrIX A33E	5.22	4.95	0.54
Commercial Absorbia GTO	5.22	5.20	0.03

Table 8. Lead Uptake for Various Experimental Materials
(Absorbent 0.025 g, 50 mL solution, and 6 minutes time)

Sample	Initial Concentration (mg/L)	Final Concentration (mg/L)	Lead (Pb) Loading (mg/g)
Birch wood hemicellulose citrate-chitosan	13.72	10.22	6.85
Mixed hardwood hemicellulose citrate-chitosan	13.72	10.53	6.23
Switchgrass hemicellulose citrate-chitosan	13.72	10.17	6.95

Table 9. Cadmium Uptake for Various Experimental Materials
(Absorbent 0.025 g, 50 mL solution, and 6 minutes time)

Sample	Initial Concentration (mg/L)	Final Concentration (mg/L)	Cadmium (Cd) Loading (mg/g)
Birch wood hemicellulose citrate-chitosan	5.33	5.13	0.40
Mixed hardwood hemicellulose citrate-chitosan	5.33	5.14	0.38
Switchgrass hemicellulose citrate-chitosan	5.33	5.06	0.53

Table 10. Selenium Uptake for Various Experimental Materials
(Absorbent 0.025 g, 50 mL solution, and 6 minutes time)

Sample	Initial Concentration (mg/L)	Final Concentration (mg/L)	Selenium (Se) Loading (mg/g)
Birch wood hemicellulose citrate-chitosan	5.47	5.02	0.85
Mixed hardwood hemicellulose citrate-chitosan	5.47	5.34	0.25
Switchgrass hemicellulose citrate-chitosan	5.47	5.32	0.29

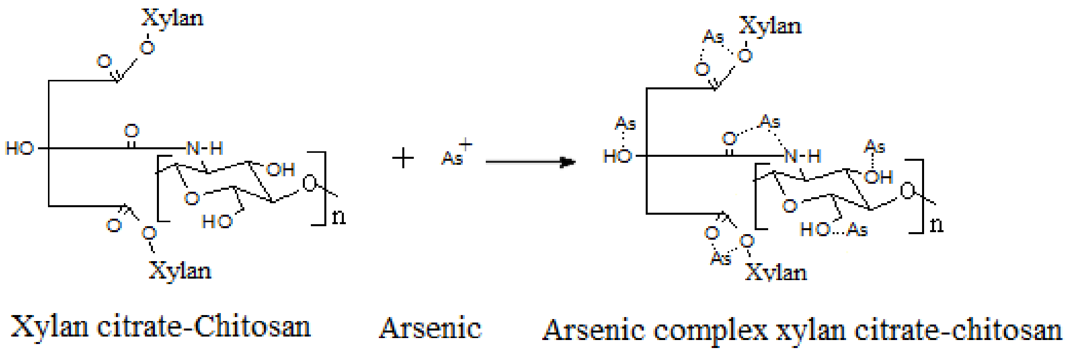


Figure 5. Possible schematic of the arsenic complex with xylan citrate-chitosan foam.

The carbohydrate-citrate-chitosan materials are very effective at binding lead. They take up in general 10 times as much compared to other heavy metals. The carbohydrate-citrate-chitosan foam was also effective at binding cadmium and selenium. This is significantly different performance when compared to traditional metal binding agents. This wide-range activity makes our materials attractive for water treatment applications.

REPORT ON TASK 2

Task 2: Define Effective, Inexpensive Routes to Produce High-Performance Hemicellulose Citrate-Chitosan Hydrogel Particles with Various Compositions and Structures

During this project, we have manufactured material in the form of particles. This was accomplished through two different processes. The first process involved generating the foams in the traditional manner, including freeze drying. The particles were then cryo-crushed using liquid nitrogen and were sent to Foamulations, LLC (Millersville, MD), where they were applied to a reticulated synthetic foam. The particles were tested in the lab for arsenic and salt uptake and were found to perform similarly to the native foamed materials.

A second process was evaluated using the same reaction scheme as in previous work. However, the freeze-drying step was eliminated. The material was instead dried in an oven at 70 °C until dry (about 4 hours). These materials were then mechanically ground. This process is much less equipment-intensive and allowed us to produce >500 g of starch citrate chitosan for testing. This material was sent to Foamulations, LLC for coating onto the reticulated foam. Reticulated foams were produced but the company has not shared the results of its testing. It is believed that the performance of the foam is similar to that of the individual particles.

The individual oven-dried particles absorbed less salt than the freeze-dried particles and foams (Figure 6). The major difficulty in processing this material was an increased solubility. Note that the untreated pulp does pick up salt appreciably.

One of the simplest methods for reducing the costs of the foam was to introduce pulp fiber into the foams. Figures 7 and 8 below show a comparison of the foam structure and absorption of water and saline with varying amounts of pulp added to the foam. It is found that about 50 percent wood pulp fiber can be added to the foam without a significant change in the performance of the foam. This indicates that an increased wetting phenomenon through higher specific surface area originating from the fibers may be affecting the ability of the foam to perform.

Thus, we have developed three methods for reducing the cost of the foam. First, we can attach the foam to a reticulated foam structure to reduce the cost of generating the foam. Second, we can eliminate the need for freeze drying, but this then requires the addition of a washing step. Lastly, we can add pulp to the foam to reduce the overall cost without decreasing performance at up to 50 percent addition.

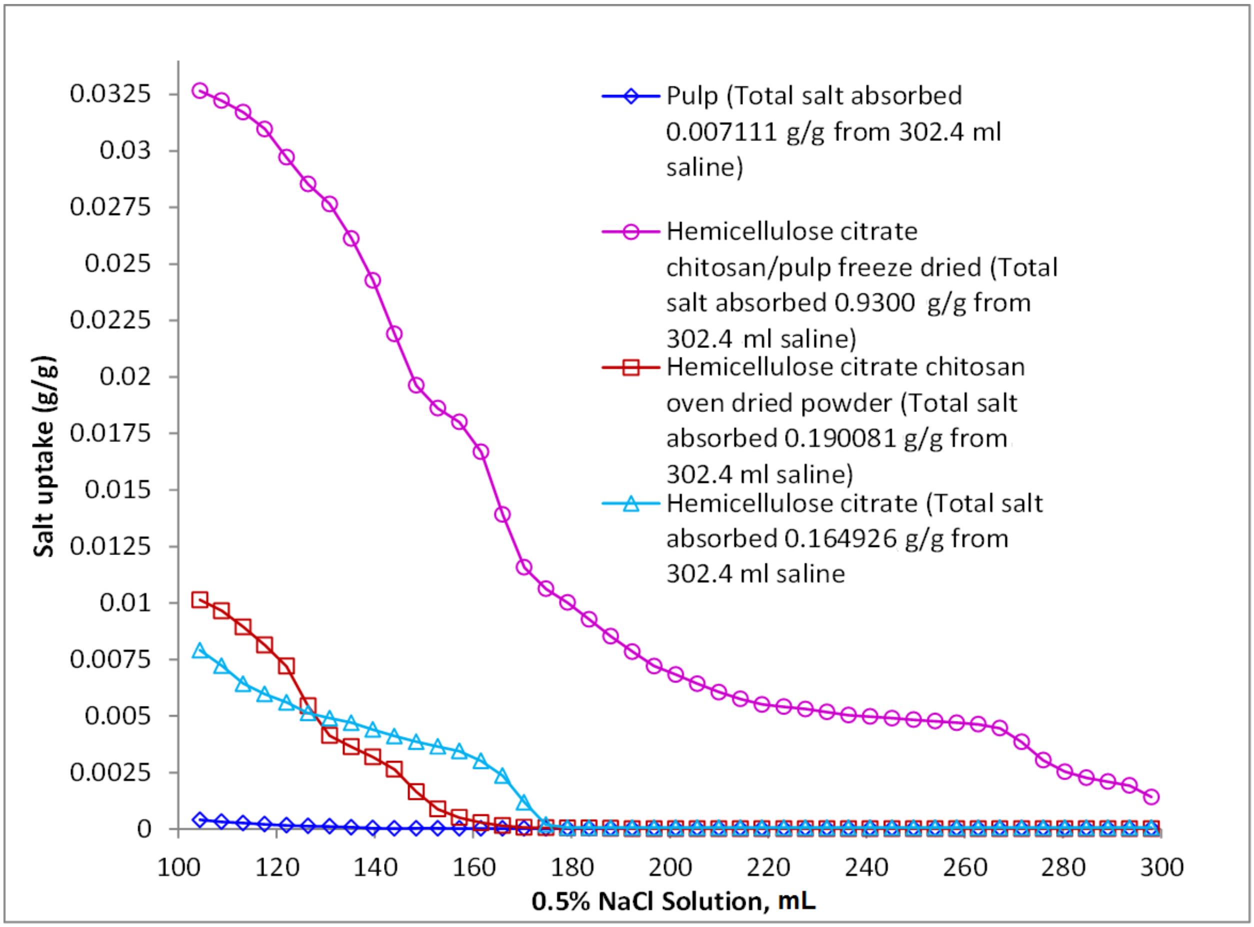


Figure 6. Salt uptake for raw pulp, HCCC freeze dried, HCCC oven dried, and HC.

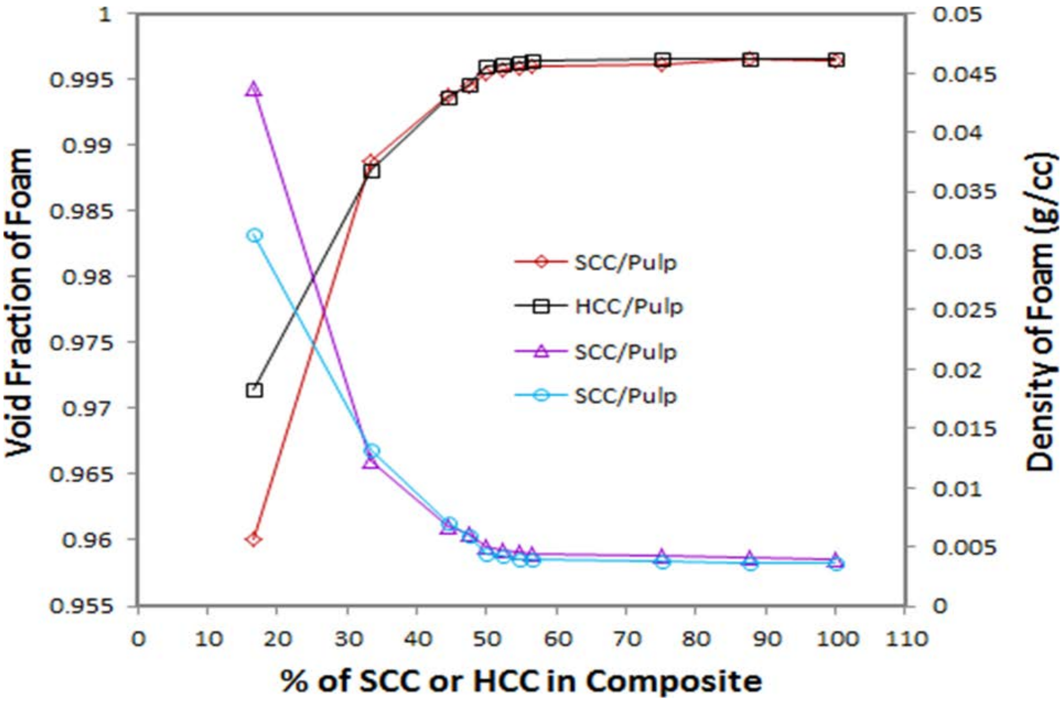


Figure 7. Void fraction and density of foam versus the mass percent of SCC or HCC in composite.

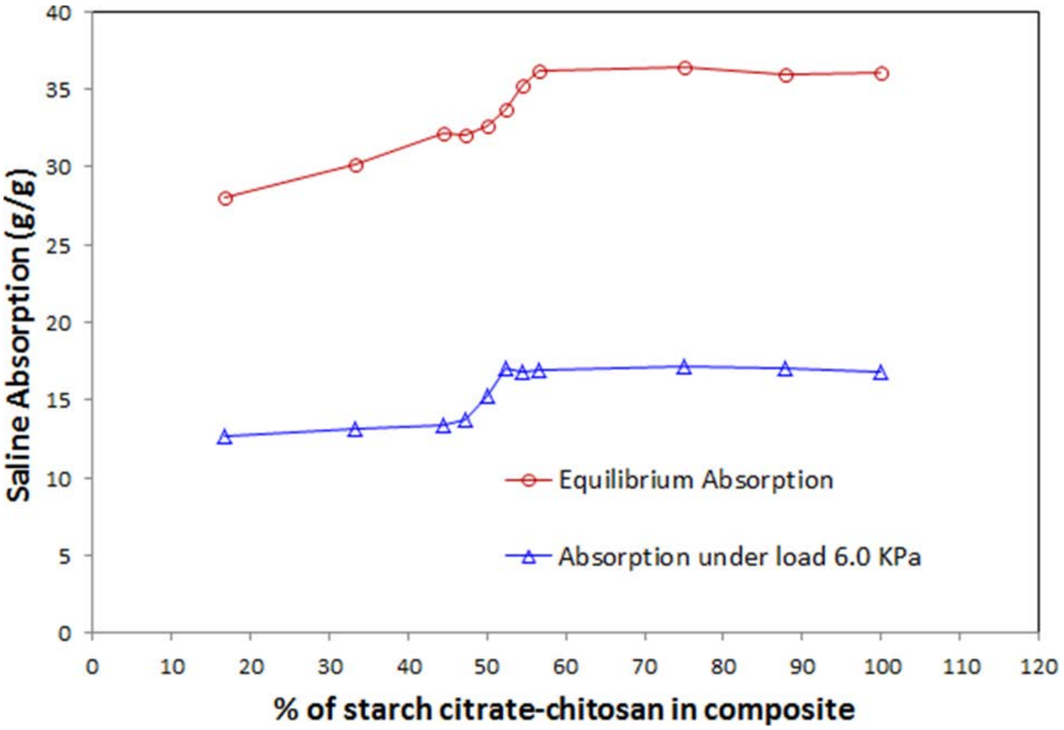


Figure 8. Saline absorption for various ratios of starch citrate-chitosan and pulp.

REPORT ON TASK 3

Task 3: Characterize the Desalination of Water Using These Hydrogel Particles

The amount of salt taken up under various conditions and for a variety of material compositions was determined. Three different techniques were used for this determination. In one method, the conductivity of the saline solution was determined before and after exposure to our materials, and then a calibration line was used to determine salt concentrations and thus the amount of salt uptake. The second method involved weighing the salt that remained in the solution as determined by evaporation (gravimetric). The third method used TGA to determine the salt concentration by thermally decomposing the organic part of the sample. Details are reported below.

A. Salt Uptake

The effect of salt uptake results at various molecular weights of chitosan (deacetylated chitin)-hemicellulose citrate foam is shown in Table 11. High-molecular-weight chitosan-hemicellulose citrate foam uptakes significantly more salt than foams made with low-molecular-weight chitosan.

Table 11. Salt Uptake Deacetylated Chitin-Extracted Hemicellulose Citrate Foam Samples of Various Molecular Weights

Molecular weight of chitosan sample (g/mol)	Salt uptake in exhaust bath (g/g) (3.5% NaCl solution)	Salt uptake (g NaCl/g foam), TGA heating in air (3.5% NaCl solution)
2,281,000	1.60	1.30
2,549,000	1.52	1.18
381,000	0.36	0.75
267,000	0.22	0.70

The chitosan (4-hour treated) was reacted with extracted hemicellulose (birch wood xylan) citrate to produce foam. Three different methods were used to determine salt uptake such as gravimetric, conductivity, and thermo-gravimetric analysis. Samples of ~0.025 g were weighed and placed in a pre-weighed tea bag. The sample and tea bag were then soaked for 20 minutes in 25 mL of 3.5-percent NaCl solution. The foam was then dried overnight at 105 °C, and the weight gain in the sample was taken to be the salt uptake.

Salt uptakes of 1.12 and 1.24 g/g were determined by gravimetric process for the chitosan hemicellulose-citrate foam and the chitosan hemicellulose-citrate/pulp (52:48) foam, respectively (Table 12). Conductivity tests of the initial and final solution after exposure to the two foams indicated that the chitosan hemicellulose-citrate foam and the chitosan hemicellulose-citrate/pulp foam contained, respectively, 0.96 and 1.02 g/g of NaCl. To confirm, the samples were tested by TGA upon heating to 600 °C at 10 °C per minute, under nitrogen. The salt content of the sample was determined by subtracting a control residual char from the residual char weight of the sample plus the salt. (See Figure 9.) The salt content according to this method was found to be 1.37 and 1.08 g/g, respectively, for chitosan hemicellulose-citrate foam and chitosan hemicellulose-citrate/pulp foam (Table 12).

Table 12. Salt Uptake of Deacetylated Chitin-Extracted Hemicellulose (Xylan) Citrate Foam

Hydrogel (Absorbent)	**Salt uptake in exhaust bath (g NaCl/g foam) (3.5% NaCl solution)**	**Salt uptake in conductivity test (g NaCl/g foam) (3.5% NaCl solution)**	**Salt uptake (g NaCl/g foam), TGA heating in air (3.5% NaCl solution)**
Commercial chitosan-commercial hemicellulose (birch wood xylan) citrate foam	0.88	0.93	0.79
Chitosan-extracted hemicellulose (birch wood xylan) citrate foam	1.12	0.96	1.37
Chitosan-extracted hemicellulose (birch wood xylan) citrate/pulp composite	1.24	1.02	1.08

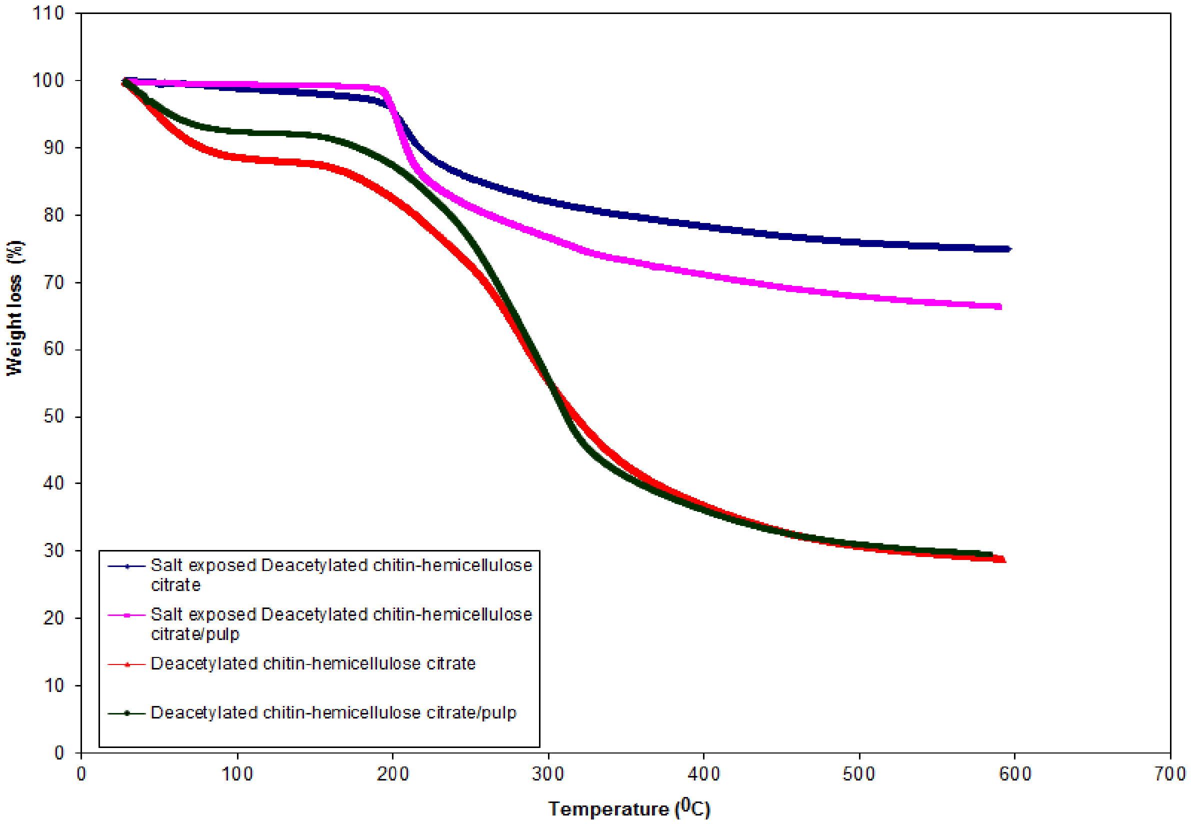


Figure 9. TGA of salt-exposed chitosan hemicellulose-citrate and chitosan hemicellulose-citrate/pulp foam (under nitrogen).

A summary of results of hemicellulose-citrate chitosan foam relative to control materials (commercial hemicellulose-citrate commercial chitosan foam) is shown in Table 13. The water absorption in both deionized water and NaCl solution was close to that of the commercial hemicellulose-citrate commercial chitosan foam. In addition, the water and saline solution absorption with birch wood extracted hemicellulose-citrate chitosan/pulp composite was higher than extracted hemicellulose-citrate chitosan foam (Table 13).

Table 13. Water and Saline Absorption for Extracted Hemicellulose Citrate-Deacetylated Chitin Foam

Sample	**DI Water Absorption (g/g)**		**Saline (3.5% NaCl) Absorption (g/g)**	
	Equilibrium Swellability	**Vacuum Filtration**	**Equilibrium Swellability**	**Vacuum Filtration**
Extracted hemicellulose citrate-deacetylated chitin foam (birch wood xylan)	27.10	6.10	34.20	7.46
Extracted hemicellulose citrate-deacetylated chitin foam (mixed hardwood xylan)	26.75	5.34	27.80	5.90
Extracted hemicellulose citrate-deacetylated chitin foam (switchgrass xylan)	27.50	6.25	34.08	7.06
Hemicellulose citrate-deacetylated chitin foam (commercial birch wood xylan)	31.00	7.00	36.00	8.20
Extracted hemicellulose citrate-deacetylated chitin/pulp foam (birch wood xylan)	31.40	7.05	38.09	8.37
Commercial super absorbent (SPA)	197.00	149.00	33.5	18.00

REPORT ON TASK 4

Task 4: Characterize the Heavy-Metal Uptake of Water Using These Hydrogel Particles

The heavy-metal uptake for a variety of metals was determined. Table 14 shows the arsenic uptake for some materials. Note that this material proved to be rather effective in removing metals from water. Results related to this task are also reported under Task 1. Please refer to that section of the report for additional results.

Table 14. Arsenic Uptake for Various Materials in a 5.625-mg/L Solution
(Absorbent 0.025 g, solution 50 mL, and soaking time 6 minutes)

Sample	Initial Concentration (mg/L)	Final Concentration (mg/L)	Arsenic Loading (mg/g)
Hemicellulose citrate-chitosan/pulp (60:40)	5.625	5.230	0.79
Starch citrate-chitosan/pulp (60:40)	5.625	5.135	0.98
Pulp	5.625	5.430	0.39
Hemicellulose citrate-chitosan	4.950	4.310	1.28
Starch citrate-chitosan	4.950	4.030	1.84

The maximum absorption can also be determined for a variety of metals from a Langmuir isotherm. This requires a number of concentrations of heavy metals to be tested. Table 15 shows results for the maximum uptake compared to commercial chelating agents.

Table 15. Equilibrium Absorption Amounts of Various Metals for Two Experimental Chelating Agents and a Commercial Metal Scavenger

Metal-Chelating Agent	As (mg/g)	Pb (mg/g)	Hg (mg/g)	Cd (mg/g)	Se (mg/g)
Hemicellulose citrate-chitosan	0	21	264	32.8	18
Starch citrate-chitosan	14	16.4	160	11.3	26
Commercial Sorba Tech 450	0	21.3	646	17.4	17.4

REPORT ON TASKS 5 AND 6

Task 5: Evaluate the Regeneration of These Materials, Making the Process Even Less Expensive

Task 6: Develop Effective Continuous Processes for Applying These Materials

Attempts were made to regenerate the foam materials after they had absorbed salt. The literature had reported that similar materials could be regenerated by varying the pH of the solutions flowing past the foams. Our results indicated that once the foam absorbs the salt it is very difficult to remove it from the foam. Furthermore, we have designed a bench-scale continuous treatment apparatus. This apparatus proved to be successful in treating water and for evaluating samples. Details are reported below.

A. Regeneration and Continuous Treatment

Regeneration of the foams was attempted using HNO_3 at pH 2.5 for 3 hours at room temperature. We placed 5 g material into a 250-mL beaker and then added 200 mL of 2.5-pH nitric acid solution. The mixture was held for 3 hours at room temperature and then washed with DI water until the material's pH was 5. After the wash, the material was dried at 60 °C overnight before being tested in repeat salt absorption trials.

Result and Discussion

Figure 10 shows the conductivity of the outlet flow of salt solution that has flowed past regenerated and non-regenerated foam materials. Hence, it inversely reflects the salt uptake of those materials. The experiment was conducted using the apparatus for Task 6. Figure 10 indicates that the salt uptakes of the regenerated starch citrate-chitosan powder and the regenerated starch citrate-chitosan/pulp composite were both very low compared to the uptakes of the original unused powders. This regeneration technique does not have the ability to regenerate the salt uptake properties.

B. Bench-Scale Treatment System

We have assembled and calibrated a continuous flow-through laboratory-scale system to evaluate our materials for salt uptake (Figure 11). The system has two continuous-flow stirred-tank reactor feed tanks with controlled flow rate peristaltic pumps. The feed passes through an in-line conductivity meter prior to entering the absorption vessel. The absorption vessel has filters in the inlet and outlet to contain the materials tested. Another in-line conductivity meter exists on the outlet of the absorption vessel. Changes in conductivity detected between the inlet and outlet sensors are converted to changes in salt concentration via known conductivity versus salt concentration relationships.

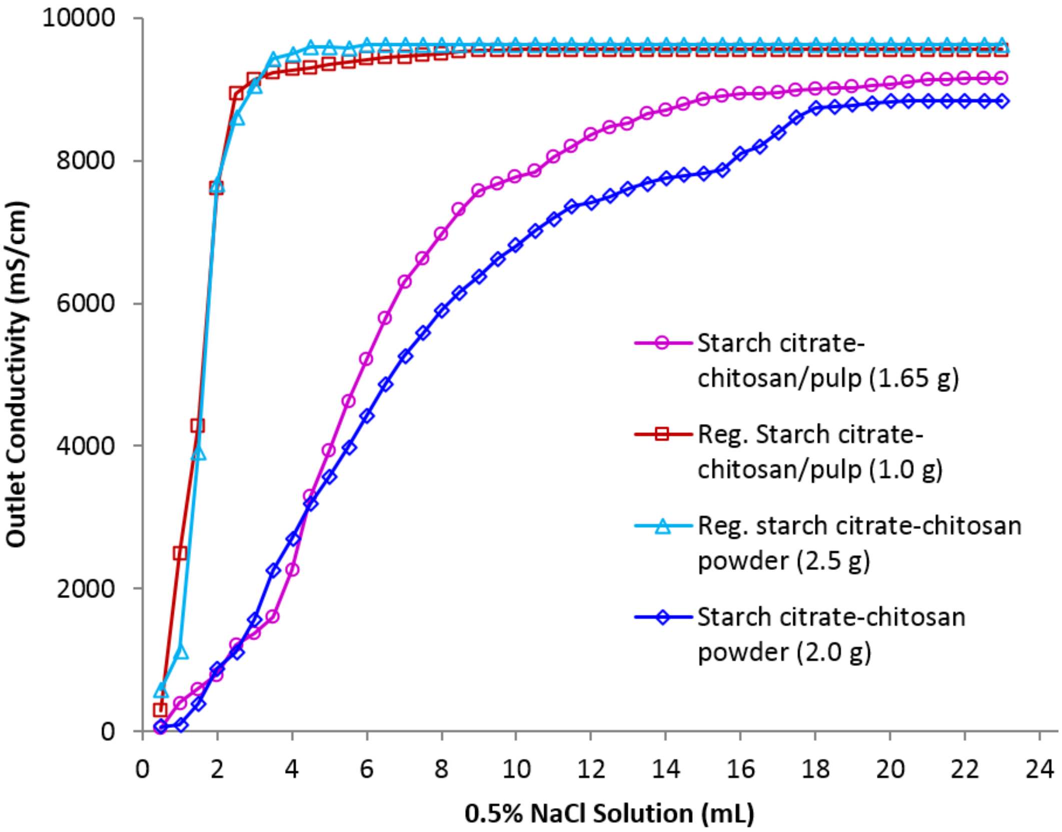


Figure 10. Salt uptake of regenerated SCC powder and SCC/pulp composite. High outlet conductivity indicates that salt has not been removed by the sample.

Several experiments have been conducted in order to determine the dynamic salt absorption of our materials in a continuous flow-through operation. Figure 12 shows the results for fibers (pulp), hemicellulose citrate, hemicellulose citrate chitosan powder, and hemicellulose citrate chitosan fiber foam (freeze-dried). Note that the powders were dried in an oven and ground, not freeze-dried. Total salt uptake was determined by integrating under the curves of salt uptake versus amount of solution processed in the column.

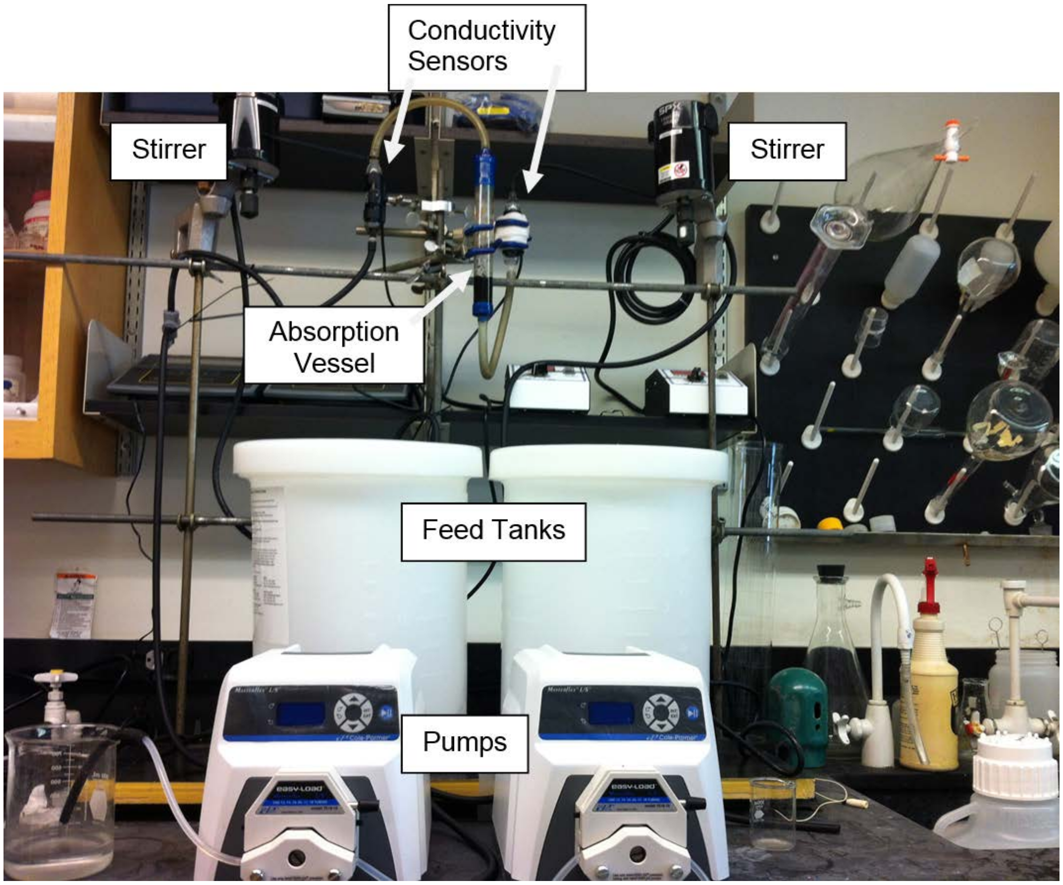


Figure 11. Experimental setup for the continuous flow-through absorption.

It is observed that the fibers alone do not remove NaCl, as expected. This is an important control for our experiments. The powders of hemicellulose citrate and hemicellulose citrate chitosan do show some salt absorption. However, about 4 times higher salt absorption is realized with the hemicellulose citrate chitosan/ pulp foam material — approximately 0.9 grams of NaCl per gram of material. This indicates that the structure of the material greatly influences the amount absorbed, and so a high-specific-area foam-fiber composite structure contributes positively to absorption.

Similar results were determined for starch structures, used as a control material to contrast with hemicellulose materials. A summary of the overall absorption for several different materials tested in the dynamic tester is shown in Table 16.

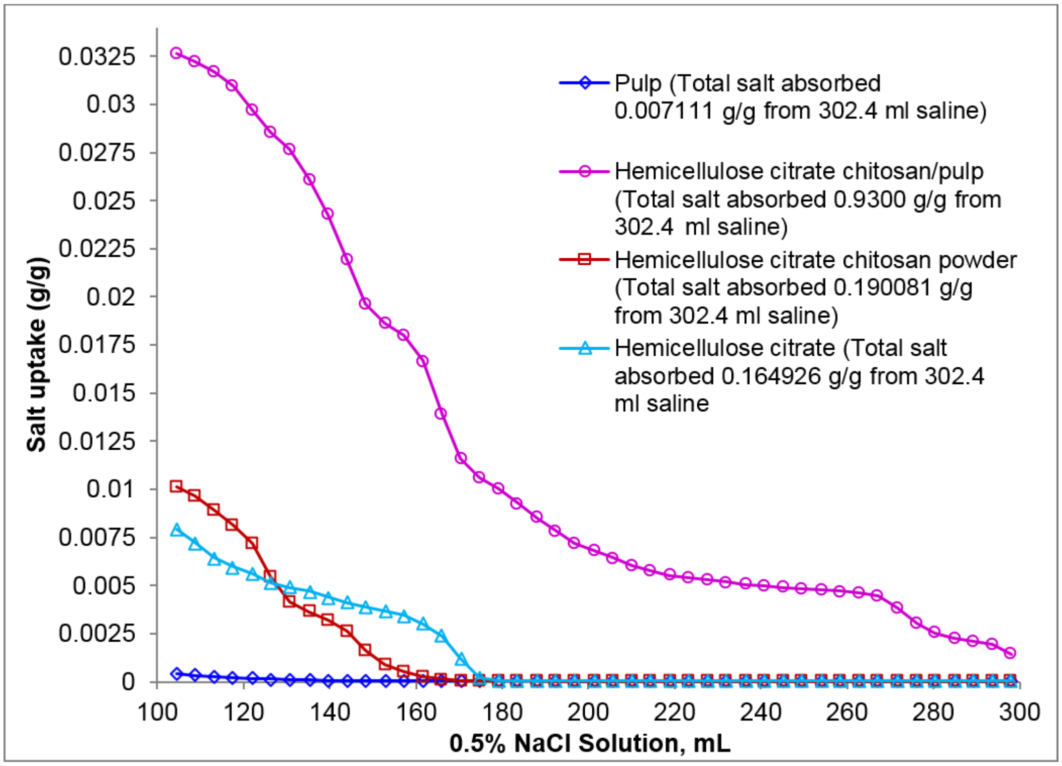


Figure 12. Salt uptake versus volume of 0.5-percent NaCl solution passed through various materials.

Total salt uptake shown in the legend for each sample.

Table 16. Summary of Salt Uptake for Various Materials, as Determined Using the Continuous Flow-Through Absorption Apparatus

A total of about 300 mL of 0.5% NaCl solution was passed at 8.8 mL/min through the absorption material.

Sample	Total Salt Uptake (g salt/g sample)
Hardwood bleached fibers	0.0071
Hemicellulose citrate particles	0.1649
Hemicellulose citrate-chitosan powder	0.1900
Hemicellulose citrate-chitosan powder reuse (1st wash)	0.1853
Hemicellulose citrate-chitosan powder reuse (2nd wash)	0.1767
Hemicellulose citrate-chitosan/pulp composite	0.9300
Hemicellulose citrate-chitosan/pulp composite reuse (1st wash)	0.6530
Hemicellulose citrate-chitosan/pulp composite reuse (2nd wash)	0.5897
Starch citrate	0.1229
Starch citrate-chitosan powder	0.1358
Starch citrate-chitosan powder reuse (1st wash)	0.0756
Starch citrate-chitosan powder reuse (2nd wash)	0.0713
Starch citrate-chitosan/pulp composite	0.3427
Starch citrate-chitosan/pulp composite reuse (1st wash)	0.2666
Starch citrate-chitosan/pulp composite reuse (2nd wash)	0.2315

We have used the continuous flow-through equipment to evaluate regeneration methods to reuse our materials after they have absorbed salt. The first method investigated was to try to wash the materials with deionized water. This approach was not found to be practical in application but was of interest to understand how tenaciously the NaCl is held by the samples. To evaluate, hemicellulose citrate chitosan fiber material was exposed to 300 mL of the 0.5-percent NaCl solution in the continuous absorption apparatus and then rinsed (within the apparatus) with copious amounts of water until no NaCl was detected in the wash water.

Figure 13 shows the outlet concentration of NaCl as a function of the volume of 0.5-percent NaCl passed through the fresh hemicellulose citrate chitosan (HCCC) fiber material (squares) and the same material after one washing (triangles). It is evident that the simple DI water washing does not regenerate the same performance as seen for the fresh material. The results indicate that a significant fraction of NaCl is strongly bound to the material, whereas another fraction may be rinsed by DI water. Table 16 also shows similar results for starch-based materials.

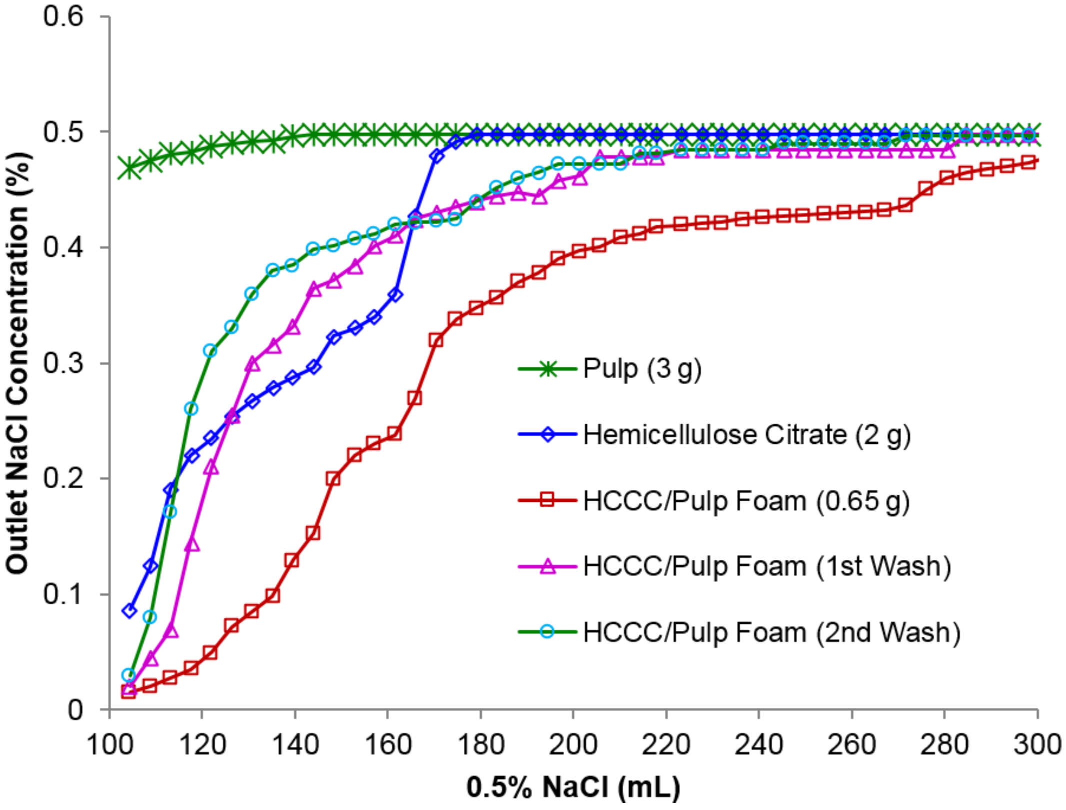


Figure 13. Outlet salt concentration versus volume of 0.5-percent NaCl solution passed through various materials.

Note that the outlet concentration is reported, not the gram-per-gram NaCl absorption, as was shown in Figure 12. Pulp and hemicellulose citrate are shown for comparison, but were charged at much higher levels.

REPORT ON TASK 7

Task 7: Summarize the Economic Viability of These Processes and Indicate Technologies in which They Surpass Existing Technologies for Economic and Other Reasons

This task was first evaluated by estimating the cost of the composite material needed for desalination. The cost to treat a gallon of water was compared to a literature cost using reverse osmosis of seawater. The basic assumptions used in the model for determining the cost of composite material are shown in Table 17.

Table 17. Basic Inputs for Cost Estimation of Composite Raw Material

Cost of Composite Raw Materials		
Softwood pulp	$500	/ton
Citric acid	$0.25	/lb
Catalyst	$0.10	/lb
Hemicellulose	$1.00	/lb
Starch	$0.35	/lb
Chitosan	$1.00	/lb
Energy		
Electric rate	$0.10	/kWh
Energy used in freeze-drying	0.2	kWh/lb
Energy cost per pound	$0.04	/lb
Capital Costs		
Initial investment	$3,000,000	
10-year depreciation	$300,000	/yr
Plant capacity	2,000,000	lbs/yr
Capital costs per pound	$0.15	/lb
Operating Costs		
Labor (fully loaded)	$1,000,000	/yr
Operating and maintenance at 10% of capital	$300,000	/yr
Plant capacity	2,000,000	lbs/yr
Operating costs per pound	$0.65	/lb

Using these inputs, one can evaluate the effect of composition on the overall cost of the material. Using the assumption of a $3 million capital investment in an existing chemical manufacturing plant with a capacity of 1,000 tons per year and raw material costs as shown in Table 17, the cost sensitivity for pulp substitution and starch substitution identified in this research can be evaluated.

Figure 14 shows the effect of substituting up to 50 percent pulp fiber into the material when the basic composition is:

Composite Composition	*Mass Fraction*
Softwood pulp	0.5
Citric acid	0.1
Catalyst	0.1
Hemicellulose	0
Starch	0.15
Chitosan	0.15

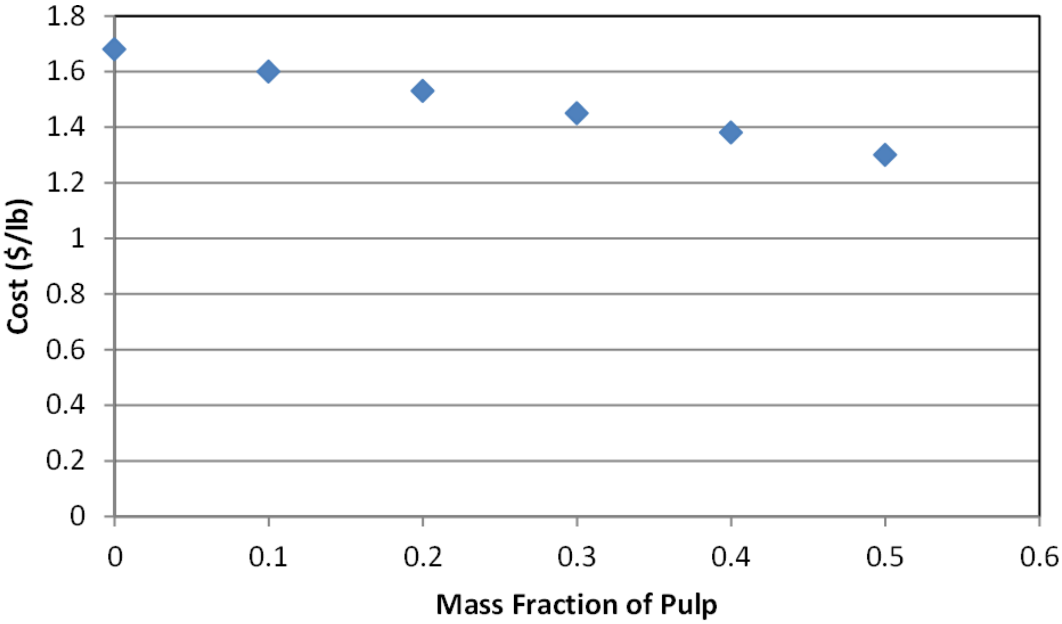


Figure 14. Cost per pound of material with increased levels of pulp substitution.

Research in this project has shown that up to 50 percent pulp can be added to the material with no loss in the performance of the material. This results in a $0.38 per pound savings. Thus, it is highly advisable that pulp be substituted up to 50 percent. Additionally, it has been shown that starch will also work in this system. Figure 15 shows the effect of substituting starch for hemicellulose. Note that 15 percent substitution means that 100 percent of the hemicellulose has been removed. This substitution would represent an additional cost savings of $0.10 per pound. However, work has shown that the starch-bearing material may not be as effective as the material made with hemicellulose. Thus, further trials would have to be conducted to see the balance between reduced performance and cost savings.

The manufacturing costs make up about two-thirds of the total cost of the material (Figure 16). One concern about the manufacture of this product was the need for a large-scale freeze-drier. Research showed that oven-dried powders could be produced but that they would function at a reduced capacity. Thus, the cost savings must be significant for the oven-drying method to be explored. One could reduce the capital investment from $3 million to $2 million by eliminating the need for a freeze-dryer. This assumes that the plant manufacturing this material will have existing oven-driers that could be used. This would translate into a cost reduction of $0.10 per pound. This decrease in cost is not likely large enough to offset the reduced efficiency of the material.

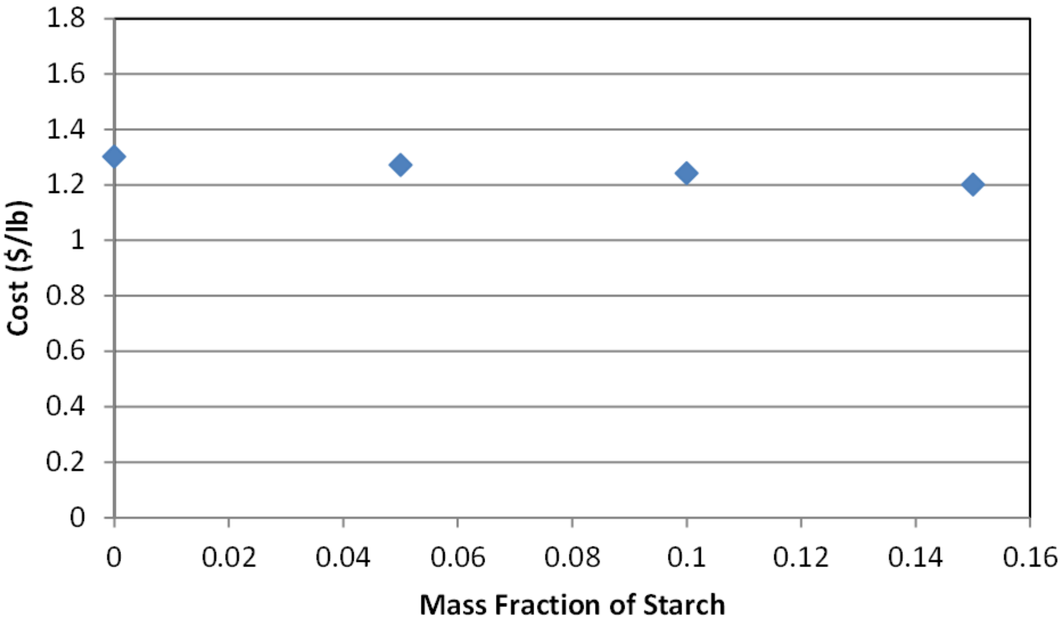


Figure 15. Cost per pound of the material as starch is substituted for hemicellulose.

Note that 0.15 mass fraction of starch represents a composite with 50 percent pulp and no hemicellulose.

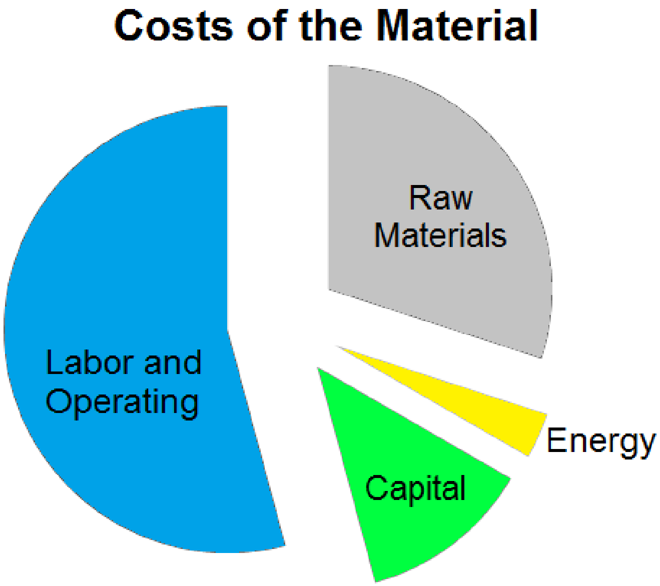


Figure 16. Chart showing the proportion of each component's contribution to the overall cost.

At the minimum cost of $1.20 per pound for freeze-dried materials, one can assume that about 1 gram of salt is taken up by 1 gram of material when the salt concentration is 3.5 percent (near that of sea water). Based on this estimate, about 0.25 pounds of material would be needed to desalinate a gallon of water. The cost of the material alone would be ~$0.35 per gallon. This does not include water treatment facilities, etc. Thus, one would not expect that this material would be useful in large-scale desalination. For example, the cost of a reverse-osmosis system at the municipal scale is reported by U.S. Army Corps of Engineers to be about $0.006 per gallon.

However, there are a number of markets in which this material may be useful. These include emergency water treatment applications where electricity is not available. For example, use by soldiers in a survival situation, emergency kits for offshore boaters, or kits for natural disasters such as earthquakes, tsunamis, etc.

The most promising market for this material is for the treatment of high salt concentration solutions. For example, in the hydro-fracturing industry, each well may produce up to 1 million gallons of water that has a 30-percent salt concentration. Current treatment technologies are not effective for treating this water. The water is currently disposed of in municipal water systems, where the costs for transportation and treatment are both very high. Using this material, one may be able to treat the brine solution on site, as the technology is effective at high salt concentrations. The principal investigators for this report are currently partnering with a start-up company called Tethys to bring this technology to the hydro-fracturing industry.