

## FLAX SHIVE AS A SOURCE OF ACTIVATED CARBON FOR METALS REMEDIATION

Wayne E. Marshall<sup>a</sup>, Lynda H. Wartelle<sup>a</sup>, and Danny E. Akin<sup>b\*</sup>

Flax shive constitutes about 70% of the flax stem and has limited use. Because shive is a lignocellulosic by-product, it can potentially be pyrolyzed and activated to produce an activated carbon. The objective of this study was to create an activated carbon from flax shive by chemical activation in order to achieve significant binding of selected divalent cations (cadmium, calcium, copper, magnesium, nickel, zinc). Shive carbons activated by exposure to phosphoric acid and compressed air showed greater binding of cadmium, copper, nickel or zinc than a sulfuric acid-activated flax shive carbon reported in the literature and a commercial, wood-based carbon. Uptake of calcium from a drinking water sample by the shive carbon was similar to commercial drinking water filters that contained cation exchange resins. Magnesium removal by the shive carbon was greater than a commercial drinking water filtration carbon but less than for filters containing cation exchange resins. The results indicate that chemically activated flax shive carbon shows considerable promise as a component in industrial and residential water filtration systems for removal of divalent cations.

*Keywords:* Flax shive, Activated carbon, Metal ion, Phosphoric acid activation

*Contact information:* a: USDA-ARS, Southern Regional Research Center, 1100 Robert E. Lee Blvd., New Orleans, LA 70124 USA; b: USDA-ARS, R. B. Russell Research Center, 950 College Station Road, Athens, GA 30605 USA

\*Corresponding author: [danny.akin@ars.usda.gov](mailto:danny.akin@ars.usda.gov)

### INTRODUCTION

Flax (*Linum usitatissimum* L.) is a versatile crop that supplies both fiber and seed (i.e., linseed) for important industrial applications (Domier 1997). The desire for natural fibers to replace glass fiber and the promotion of linseed and linseed oil for nutraceutical uses bodes well for increased flax production. Bast fiber and linseed already have value-added markets (Sharma 1992), and interest is increasing for finding value-added uses of the by-products, such as the non-fiber part of the stem, to improve the economics (Domier 1997).

Flax stems constitute the source of bast fibers, which are used in a variety of applications (textiles, composites, specialty paper). To obtain these bast fibers, flax straw is first retted, in which fiber is separated from non-fiber components such as shive. Shive is the woody, lignified inner tissues of the stem and is a by-product of fiber production. Flax fiber constitutes about 25-30% of the stem (Stephens 1997). Therefore, a large amount of shive is available after fiber processing. With estimates of 1 million tons of flax straw available annually from linseed production (Dormier 1997), about 700,000 tons of shive could be available for a variety of uses.

Traditionally, shive is considered a waste product and as such has limited value or is used in low-value applications such as chip board, animal bedding, and burning for thermal energy (Sankari 2000; Sharma 1992). Sharma (1992, 2004) reported that upgrading shive using lignin-degrading, white rot fungi, which include edible mushrooms, was a promising use. The large amount of shive available, the collection and concentration at fiber processing plants, and the requirement to transport waste shive away all call for research into value-added uses. Certainly, the need to make use of this potential resource is recognized (Domier 1997), and internet searches list horse bedding ([www.ecolit.com](http://www.ecolit.com)) and reinforced thermosetting ([www.freepatentonline.com](http://www.freepatentonline.com)) as diverse potential uses. Higher value uses may be possible with technology, such as extraction of aromatics (Kim and Mazza 2006) for a variety of uses such as antioxidants and antimicrobial compounds.

Studies by Cox et al. (1999, 2000) and by El-Shafey et al. (2002) demonstrated that flax shive could be converted to carbonaceous material by contact with sulfuric acid. This material used to sorb a variety of divalent cations. A more recent investigation by Cox et al. (2005) showed that a carbon sorbent prepared from flax shive could adsorb precious metals, such as silver. Two papers by Williams et al. (1997, 1998) used waste linseed straw to adsorb copper, nickel and cadmium in a semi-continuous batch adsorption system. Adsorption of the three metals by linseed fiber was not as effective as using a seaweed waste product under similar experimental conditions.

In addition to carbonized flax shive, several other woody plant straw sources have been successfully converted to activated carbon for the removal of metal ions. Johns et al. (1998) used rice straw and sugarcane bagasse and activated this material for carbon production by steam, carbon dioxide, or carbon dioxide plus 38% oxygen. Carbon with the greatest adsorption towards copper ion was produced by activation with carbon dioxide followed by oxidation with 38% oxygen.

Metal ion adsorption of activated carbon from agricultural waste sources can also be enhanced by pyrolysis/activation with phosphoric acid and breathing air (Toles et al. 1998). The activated carbons thus produced can be used to remove high levels of metal ions from aqueous solution.

The objectives of this study were to investigate flax shive prepared by two different retting treatments as a source of activated carbon for metal ion adsorption and to compare our results with the results of Cox and co-workers who used a different carbon activation process. Flax shive carbons were prepared in our laboratory by chemical activation with phosphoric acid and compressed air and their metal ion adsorption properties evaluated.

## EXPERIMENTAL

### Materials

Flax shive was collected after processing retted flax stems from the USDA Flax Fiber pilot plant, Clemson, SC. Sources of shives included: 1) dew-retted flax, and 2) experimental enzyme-retting using a commercial pectate lyase and chelator (Akin et al., in press). Dew-retting, which depends upon naturally occurring fungi to colonize and partially degrade flax stems, is the primary commercial method used to separate fiber

from shive. Enzyme-retting is an experimental process to provide a more consistent fiber. Waste shive derived from both retting processes was sifted through a sieve with 20 mm x 4 mm openings and then through a sieve with 5 mm diameter openings to remove fiber. Cleaned shive passing through the sieves was milled through a Wiley mill with a 2 mm mesh screen and constituted the material for activated carbon.

Norit C was purchased from Norit Americas Inc. (Marshall, TX). It is a wood-based carbon manufactured by a phosphoric acid activation process. The sample as received contained residual phosphoric acid. Thus, the carbon was treated with several washings of hot water to remove the residual acid before use in this study.

Three commercial drinking water filtration cartridges were used and were purchased at local retail outlets. PÜR RF (Replacement Filter) cartridges are comprised of a coal-based carbon and are used in point-of-use applications to purify residential tap water. PÜR PF (Pitcher Filter) cartridges contain mostly cation exchange resin with some carbon included. They are particularly effective at removing lead from drinking water in a pitcher filter configuration. Both products are made by PÜR, Minneapolis, MN. Brita PF is a water filtration product similar to PÜR PF in composition and use. It is made by Brita Products Company, Oakland, CA. The synthetic cation exchange resin IRC86 was purchased from Supelco, Inc., Bellefonte, PA. According to the manufacturer, IRC86 is used to remove hard water cations to soften water for various industrial processes. All commercial adsorbents were dried in a forced air oven at 60°C for 12 hours before adsorption studies were conducted.

## Methods

Particles of non-carbonized shive and phosphoric acid-activated shive carbon were mounted on carbon tabs on SEM stubs, coated in a sputter coater with gold, and viewed in a JEOL JSM 5800 scanning electron microscope at 15 kV.

Proximate analyses of dew-retted and enzyme-retted flax shives were carried out by Eurofins Scientific, Inc. (Des Moines, IA) using standard AOAC methods.

Flax shive activated carbon was made by placing 100 g of 0.85 to 2.00 mm shive particles into a large porcelain evaporating dish. For phosphoric acid activation, 100 g of 30% (w/w) phosphoric acid was added to the 100 g of shive, mixed, and the mixture allowed to stand overnight at room temperature in order to imbibe the phosphoric acid. The evaporating dish was placed in a retort contained within an industrial box furnace (Lindberg/Blue M, Watertown, WI) and heated to 450°C for 4 hr under a flow of compressed air. Compressed air was introduced into the retort at a rate of 40 mL/min.

Activated carbons were allowed to cool overnight in the furnace. The carbons were weighed to calculate an activation yield:

$$\% \text{ activation yield} = (\text{wgt. of carbon from furnace} / \text{wgt. of shive}) \times 100. \quad (1)$$

Phosphoric acid-activated carbons were washed several times with water at 80-90°C to remove excess acid. The carbons were washed until no lead phosphate precipitate was observed when a 0.08 M solution of lead nitrate was added to the wash solution. Washed samples were collected on a 0.18 mm US standard sieve. Carbons were dried at 110°C for 2 hr. The carbons were weighed to determine final yield:

$$\% \text{ final product yield} = (\text{wgt. of washed carbon} / \text{wgt. of shive}) \times 100 \quad (2)$$

BET (Brunauer-Emmett-Teller) surface area was determined from nitrogen adsorption isotherms obtained at  $-196^{\circ}\text{C}$  using a Micromeritics Gemini surface area analyzer (Norcross, GA). Surface areas were calculated using the BET equation supplied in the Micromeritics software.

Twenty-five mL of 20 mM solutions of the metal ions cadmium, copper, nickel and zinc were prepared in individual beakers and mixed with 0.25 g of activated carbon. The solutions were prepared by dissolving the metal salts in 0.07 M sodium acetate-0.03 M acetic acid buffer at pH 4.8. The slurry was stirred for 24 hr at 300 rpm and  $25^{\circ}\text{C}$  using Teflon stir bars in order to achieve equilibrium between adsorbed metal ion and metal ion free in solution. The pH at the beginning and end of the experiments was recorded and normally differed by about  $\pm 0.2$  pH units.

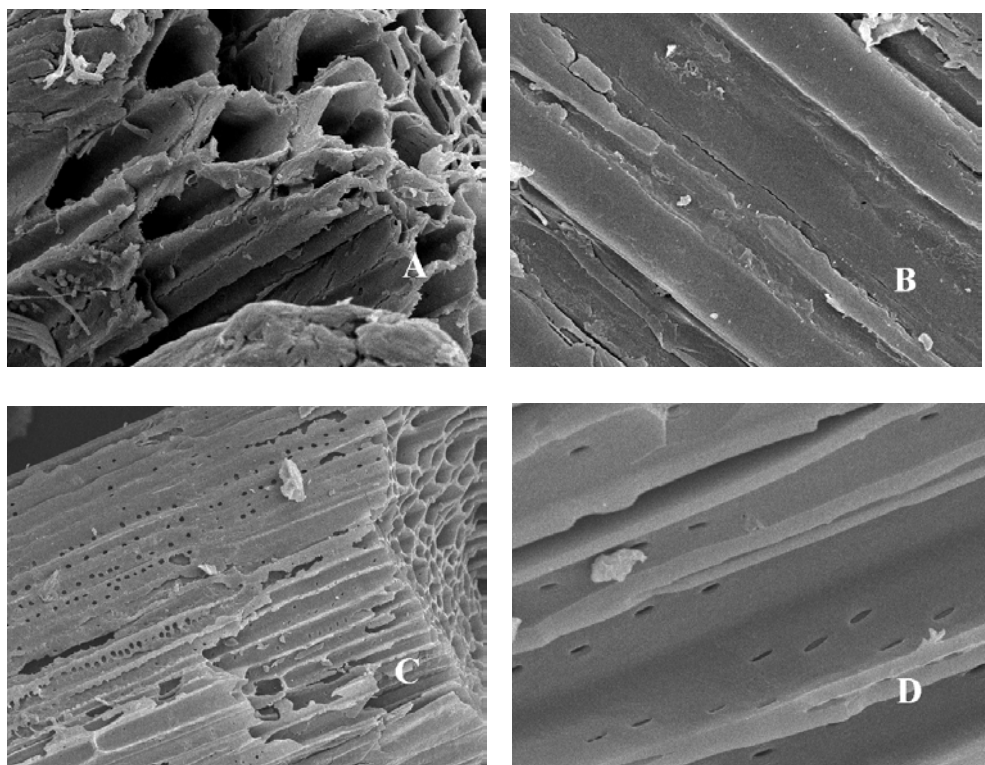
At the conclusion of the adsorption experiments, an aliquot of control solution with no carbon or experimental carbon sample was drawn into a disposable syringe and filtered through a  $0.22 \mu\text{m}$  Millipore filter (Millipore Corp., Bedford, MA). The filtered sample was diluted 1:100 (v/v) with 4 vol% nitric acid (Ultrapure, ICP grade) and analyzed using a Leeman Labs Profile ICP-AES (Teledyne/Leeman Labs, Hudson, NH).

To determine the adsorption of calcium and magnesium ions, a sample of drinking water was obtained from a municipality in Texas. The pH of the water before analysis was 8.4, indicating a high concentration of hard water cations. Two separate analyses of calcium and magnesium were determined on the water and the average values were 2.57 mmol/L (103 ppm) and 4.44 mmol/L (108 ppm) for calcium and magnesium, respectively. The municipal drinking water was not buffered and the pH varied in the range 6.5 to 7.5 during the adsorption studies for all sample examined. All water samples were stirred for 24 hr and determinations made on the calcium and magnesium concentrations after adsorption as described in the previous two paragraphs.

## RESULTS AND DISCUSSION

### Structure of Flax Shive and Flax Shive carbon

Scanning electron micrographs of flax shive and flax shive phosphoric acid-activated carbon are shown in Fig. 1. The non-carbonized shive is characterized by ordered rows of tubular structures involved in water and nutrient transport up the stem of the flax plant. Carbonization of the shive retains much of the tubular structure but the walls of the tubes are now punctuated by numerous oval-shaped pores. These are the macropores of the activated carbon. In many cases the macropores lead to a complex internal pore structure below the carbon surface that involve channels leading to both meso- and macropores where most of the adsorption takes place.



**Fig 1.** Scanning electron micrographs of untreated shive and phosphoric acid-activated, dew-retted shive carbon. A. Untreated fragment of shive. X 1,200. B. Enlarged area of untreated lignified cell wall showing relatively smooth surface. X 2,700. C. Fragment of shive constituting a particle of phosphoric acid-activated carbon showing numerous pits in the cell walls. X 500. D. Enlarged area of cell wall from phosphoric acid-activated shive carbon showing pitted surface. X 2,700.

### Proximate Analysis of Retted Shive

Table 1 shows the proximate analysis for samples of dew-retted and enzyme-retted flax shive. The type of retting appears to have essentially no effect on the cellulose, hemicellulose, lignin, protein and ash composition of the shive. Shive is between 70-75% lignocellulose with about 17% hemicellulose and minor amounts of protein and ash. A high lignocellulosic content coupled with low ash content makes shive a good candidate for carbonization and subsequent conversion to an activated carbon (Marshall, unpublished observations).

**Table 1.** Proximate Analysis of Dew-Retted and Enzyme-Retted Flax Shive.

| Sample ID     | Percent component (dry wgt. basis) |               |        |         |     |
|---------------|------------------------------------|---------------|--------|---------|-----|
|               | Cellulose                          | Hemicellulose | Lignin | Protein | Ash |
| Dew-retted    | 47.7                               | 17.0          | 26.6   | 3.5     | 1.0 |
| Enzyme-retted | 46.8                               | 16.7          | 24.1   | 3.7     | 2.1 |

### Properties of Activated Carbons from Retted Shive

Dew-retted and enzyme-retted shive were treated with phosphoric acid and activated. Activation yield, final product yield and BET surface area values are given in Table 2. There was little difference in activation yield between the two retting treatments. The activation yield for the phosphoric acid-activated carbon was about three times the final product yield. The additional weight is due to the presence of residual phosphoric acid in the sample. Upon removal of acid with repeated water washes, the final product yield was greatly reduced. Additionally, some carbon particles could be lost through the 0.18 mm mesh sieve and would add to the difference between activation and final product yields. BET surface area was higher in the carbon from dew-retted shive than enzyme-retted shive. Surface area differences were also reflected in a larger pore volume for the dew-retted carbon (data not shown). Although proximate analyses of the carbon precursors were similar (Table 1), differences in precursor structure due to the retting method employed could result in differences in pore structure formation. Since BET surface area is largely dependent on the presence of micropores, structural differences that encourage micropore formation would yield a higher surface area.

**Table 2.** Activation Yield, Final Product Yield and BET Surface Area of Dew-Retted and Enzyme-Retted Flax Shive Activated Carbons.

| Sample ID     | Activation yield (%) | Final product yield (%) | BET surface area (m <sup>2</sup> /g) |
|---------------|----------------------|-------------------------|--------------------------------------|
| Dew-retted    | 31.6                 | 12.1                    | 539                                  |
| Enzyme-retted | 33.3                 | 12.1                    | 305                                  |

### Metal Ion Uptake by Carbons from Retted Shive

Table 3 details the metal ion adsorption of four metal ions implicated in toxic contamination of water and wastewater (cadmium, copper, nickel, zinc). Flax shive carbons (dew- and Bioprep-retted) were compared to two other sets of carbons. One, flax shive carbons prepared by heating with sulfuric acid that was described by El-Shafey et al. (2002) and the other a lignocellulosic-based (wood) carbon (Norit C) that is commercially available. Metal ion adsorption values from the El-Shafey et al. (2002) study were selected by us to represent the highest monolayer adsorption capacities recorded in their paper consistent with a temperature of 25°C, the same temperature used in our experiments. El-Shafey et al. (2002) used solution pH values of 4-5 and solution temperatures of 25-45°C. Metal ion uptake values for all ions were greater in the phosphoric acid-activated shive carbons than for either literature values from El-Shafey et al. (2002) or from Norit C.

Only single values for metal ion adsorption were reported by El-Shafey et al. (2002) as given in Table 3. Thus, no statistical analysis could be made among all three data sets. Statistical comparisons were generated among data obtained in our laboratory only. However, in all cases, our range of adsorption values (Table 3) was still greater than those obtained by El-Shafey et al. (2002).

**Table 3.** Metal Ion Adsorption by Flax Shive Activated Carbons and a Commercial Carbon.

| Sample ID                       | Metal ion adsorption (mmol/g carbon, dry wgt. basis) |            |            |            |
|---------------------------------|--|------------|------------|------------|
|                                 | Cadmium  | Copper     | Nickel     | Zinc       |
| <u>Flax shive, PA activated</u> |  |            |            |            |
| Dew-retted                      | 0.57±0.03a   | 1.53±0 a   | 0.82±0.03a | 0.81±0.06a |
| Bioprep-retted                  | 0.53±0.03a   | 1.41±0.05b | 0.69±0.01b | 0.84±0.02a |
| <u>Flax shive, SA activated</u> | 0.40 <sup>1</sup>                                    | 0.82       | 0.57       | 0.50       |
| <u>Commercial</u>               |  |            |            |            |
| Norit C                         | 0.14±0.04b   | 0.27±0.03c | 0.33±0.03c | 0.20±0.02b |

<sup>1</sup> Values from El-Shafey et al. (2002).

PA = phosphoric acid; SA = sulfuric acid

a,b,c = Values within columns with different letters differ at  $P \leq 0.05$ . Values are from duplicate tests and were analyzed by one-way analysis of variance.

In another experiment, both experimental and commercial carbons were examined for their ability to remove calcium and magnesium ions that are responsible for hard water in both industrial and residential water supplies. In the example given (Table 4), a sample of drinking water from a Texas municipality was used that contained high levels of both calcium and magnesium ions. Based on the results from Table 3, the carbon from dew-retted shive was used, since this carbon performed better than the enzyme-retted counterpart in metal ion adsorption.

**Table 4.** Calcium and Magnesium Ion<sup>1</sup> Adsorption by a Dew-Retted Flax Shive Carbon and Commercial Carbons and/or Cation Exchange Resins.

| Sample ID                    | Metal ion adsorption (mmol/g carbon, dry wgt. basis) |                   |
|------------------------------|--|-------------------|
|                              | Calcium  | Magnesium         |
| <b>Dew-retted flax shive</b> |  |                   |
| PA activated                 | 0.19±0 a (71.5) <sup>2</sup>                         | 0.19±0.01a (41.7) |
| <b>Commercial</b>            |  |                   |
| PÜR RF                       | 0.00±0b (0.0)  | 0.04±0.03b (9.0)  |
| PÜR PF                       | 0.18±0.01a (71.7)                                    | 0.23±0.02c (52.6) |
| Brita PF                     | 0.20 ±0 .02a (78.1)                                  | 0.27±0.01c (61.2) |
| IRC86                        | 0.18 ±0.05a (71.2)                                   | 0.23±0c (52.3)    |

<sup>1</sup>The calcium and magnesium ion concentrations in the city drinking water supply were 2.57 mmol/L and 4.44 mmol/L, respectively. However, the amounts of calcium and magnesium ions in the assay solution were 0.26 mmol and 0.44 mmol, respectively.

<sup>2</sup>Values in parentheses are the percentages of calcium and magnesium ions removed from the drinking water.

a,b,c = Values within columns with different letters differ at  $P \leq 0.05$ . Values are from duplicate tests and were analyzed by one-way analysis of variance.

The experimental carbon was compared to adsorbents used in several commercial, potable water filtration systems and also to a commercial cation exchange resin used to remove hard water cations from industrial water supplies (IRC86). The shive-based carbon removed significantly more calcium and magnesium ions than the commercial potable water filtration carbon found in a PÜR RF water filtration cartridge. The experi-

mental carbon performed as well as the other three commercial adsorbents for the removal of calcium ion, but magnesium ion was removed at lower levels ( $P \leq 0.05$ ) compared to the other three commercial products. The most likely reason for the good performance of PUR PF and Brita PF is that both products are predominantly composed of cation exchange resin with added carbon. Details of the resins used in these products are not known. The industrial resin IRC86 from Rohm and Haas, is a weak cation exchange resin with carboxylic acid functional groups, which removes alkali earth cations, such as calcium and magnesium, that cause hardness in industrial water.

The use of phosphoric acid-activated carbon for drinking water purification would depend on the residual phosphorus content of the carbon. Several commercial phosphoric acid-activated carbons evaluated in our laboratory have been found to contain phosphorus as evidenced by a lead phosphate precipitate formed in the wash water with the addition of lead nitrate. The final wash water of our carbons does not yield a precipitate and thus may be safe for use in potable water filtration. Only actual use of our phosphoric acid-activated carbon as a filtration medium in a continuous drinking water filtration system and monitoring the effluent for residual phosphorus will determine its suitability for a particular filtration system.

## CONCLUSIONS

1. Flax shive, the woody, interior portion of the flax plant can be converted to activated carbon by carbonization and activation with phosphoric acid and compressed air.
2. The phosphoric acid-activated carbon proved adept at adsorption of several different metal ions.
3. This carbon outperformed a sulfuric acid-activated flax shive carbon described in the literature and two commercial carbons in metal ion adsorption and was comparable to commercial carbon/cation exchange resin mixtures for the uptake of calcium ion.
4. Shive, which is a low-value lignocellulosic by-product of the flax fiber industry, can be made into activated carbon and used in applications requiring removal of various metal ions from solution, potentially adding profit to an industry that derives little if any profit from the shive.

## DISCLAIMER

Mention of names of companies or commercial products is solely for the purpose of providing specific information and does not imply recommendation of endorsement by the U.S. Department of Agriculture over others not mentioned.



## REFERENCES CITED

- Akin, D. E., Condon, B., Sohn, M., Foulk, J. A., Dodd, R. B., and Rigsby, L. L. "Optimization for enzyme-retting of flax with pectate lyase," *Ind. Crops Prod.* (in press).
- Cox, M., El-Shafey, E., Pichugin, A. A. and Appleton, Q. (1999). "Preparation and characterization of a carbon adsorbent from flax shive by dehydration with sulfuric acid," *J. Chem. Technol. Biotechnol.* 74, 1019-1029.
- Cox, M., El-Shafey, E., Pichugin, A. A. and Appleton, Q. (2000). "Removal of mercury (II) from aqueous solution on a carbonaceous sorbent prepared from flax shive," *J. Chem. Technol. Biotechnol.* 75, 427-435.
- Cox, M., Pichugin, A. A., El-Shafey, E. I. and Appleton, Q. (2005). "Sorption of precious metals onto chemically prepared carbon from flax shive," *Hydrometallurgy* 78(1-2), 137-144.
- Domier, K. W. (1997). "The current status of the field crop: Fibre industry in Canada," *Euroflax Newsletter* 8, 8-10.
- El-Shafey, E., Cox, M., Pichugin, A. A. and Appleton, Q. (2002). "Application of a carbon sorbent for the removal of cadmium and other heavy metal ions from aqueous solution," *J. Chem. Technol. Biotechnol.* 77, 429-436.
- Johns, M. M., Marshall, W. E. and Toles, C. A. (1998). "Agricultural by-products as granular activated carbons for adsorbing dissolved metals and organics," *J. Chem. Technol. Biotechnol.* 71, 131-140.
- Sankari, H. S. (2000). "Linseed (*Linum usitatissimum* L.) cultivars and breeding lines as stem biomass producers". *J. Agron. Crop Sci.* 184, 235-231.
- Sharma, H. S. S. (1992). "Utilization of flax shive. In: Sharma, H. S. S., Van Sumere, C. F. (eds.), *The Biology and Processing of Flax*, M Publications, Belfast, Northern Ireland, pp. 537-543.
- Stephens, G. R. (1997). "Connecticut fiber flax trials 1994-1995." *The Connecticut Agricultural Experiment Station, Bull.* 946, New Haven, CT.
- Toles, C. A., Marshall, W. E., and Johns, M. M. (1998). "Phosphoric acid activation of nutshells for metals and organic remediation: process optimization," *J. Chem. Technol. Biotechnol.* 72, 255-263.
- Williams, C. J., Aderhold, D., Edyvean, R. G. H. (1997). "Preliminary study on the removal of copper, nickel and cadmium by waste linseed straw and/or dealginate," *Resour. Environ. Biotechnol.* 1(3), 227-241.
- Williams, C. J., Aderhold, D., Edyvean, R. G. H. (1998). "Comparison between biosorbents for the removal of metal ions from aqueous solutions," *Water Res.* 32(1), 216-224.

Article submitted: Dec. 15, 2006; First round of reviewing completed: Feb. 2, 2007;  
Revised version accepted: Feb. 21, 2007; Published: Feb. 23, 2007.