Wisconsin Cranberry Board Grant Report

Phase 5 Final Report: Use of Lignocellulosic Materials as Sorbents for Pesticide and Phosphate Residues

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Keywords: lignocellulosic materials, low-cost filtration sorbents, phosphate removal, bark, tail water

Support: This project was supported and funded by USDA Forest Service Forest Products Laboratory and the Wisconsin Cranberry Board.

Objectives: The objectives of this phase of the project were to

1. fabricate an improved filtration unit suitable for placement in tail water discharge culverts of a cranberry bog,
2. develop low-cost processes for converting bark into economical sorbents for removing phosphorus from water, and
3. evaluate performance of sorbents under both laboratory and field conditions.

Abstract: We previously reported [1] results from limited field trials of a bark-based filtration unit designed to remove phosphorus from cranberry bog tail water. In that report we also identifed some barriers that needed to be overcome to improve the performance of such a filtration unit. One barrier was lack of a costeffective process for large-scale conversion of bark to an efficient sorbent for phosphorus; another barrier was the inability of the filtration unit to handle high flow rates of tail water discharged from the bog. In this report we present an improved filtration unit design. Its performance in removing phosphorus from water was evaluated both in the laboratory, under controlled flow conditions, and in the field, under low flow conditions. Under laboratory conditions the filtration system performed satisfactorily, with a breakthrough volume of 176 L at a flow rate of 8 L/min. At the breakthrough point the outlet phosphorus concentration was 2.7 ppm, compared with the inlet concentration of 4.5 ppm. Results from field evaluations were inconclusive because tail water phosphorus concentrations entering the filtration unit were very low and close to the background levels of 0.35–0.45 ppm.

Justification: Cranberry growers are concerned about the environmental impact of residual pesticide and phosphate fertilizer runoff into receiving surface waters. Some growers have placed activated carbon filters in flumes and ditches to remove pesticide residues. However, there is as yet no suitable means of removing dissolved phosphorus runoff in the tail water, pointing to a need for low-cost phosphorus sorbents that are easy to dispose of at the end of their service life.

Potential benefits to the public from this project include

- protection of water resources from accumulation of pesticides and excessive amounts of nutrients, such as phosphorus and nitrogen, and
- reduced incidence and severity of forest wildfires through reduced accumulated fuel loads in overgrown forests. Conversion of undervalued forest residues, such as small-diameter thinnings, waste bark, and related sawmill residues, to valuable sorption media has the potential of providing economic incentives for reduction of fuel loads and prevention of forest wildfires.

Significance to Industry: This project is a significant contribution to the efforts of the cranberry industry to promote economical and ecologically sound production practices.

MATERIALS AND METHODS

Fabrication of filtration unit

The new filtration unit was fabricated from 16-gauge SS316 sheet metal in the shape of a half-cylindrical tray. The unit consists of three compartments that are separated by 2-mesh SS316 metal screens (Figure 1). The compartments can be filled with bark-based filtration sorbents with different chemistries and particle sizes. The unit is 72-in. long, 28-in. wide, and 14-in. high. Each compartment in the unit can hold up to 15 kg of filtration sorbent. The unit is designed to fit inside a culvert (Figure 2).

Preparation of sorbent material

Air-dried ponderosa pine (*Pinus ponderosa*) bark was milled in a hammermill equipped with a 1-in. screen. The milled bark was separated into three fractions by passing through a 6-mesh screen placed atop a 20-mesh screen. The fraction that passed through the 6-mesh but captured on the 20-mesh screen was collected and converted into a phosphorus sorbent by steam extraction followed by infusion with an alum solution. The alum-infused bark was allowed to air-dry before conditioning for 1 week in an oven at 105°C. Figure 3 shows the

Figure 1 - Unit containing bark-based filtration sorbent in each compartment

Figure 2 - Unit inside a tail water discharge culvert at a cranberry bog

Figure 3 - Separation of alum–infused bark from alum liquor

Figure 4 - Alum–infused bark before air-drying

alum-infused bark being separated from the alum liquor, and Figure 4 shows the alum-infused bark before air-drying.

RESULTS AND DISCUSSION

Laboratory experiments

Ponderosa pine bark was analyzed for aluminum (Al), calcium (Ca), iron (Fe), phosphorus (P), and sulfur (S) content before and after infusion with alum. Results are summarized in Table 1. Ponderosa pine bark contains large amounts of intrinsic calcium and trace amounts of aluminum, sulfur, phosphorus, and iron. Alum uptake after infusion is demonstrated by a large increase in aluminum and sulfur contents of the bark, accompanied by a large decrease in iron content and a relatively small decrease in calcium content. This suggests that aluminum immobilization in the bark is by iron displacement.

Table 1 - Elemental composition of ponderosa pine bark

	Composition (mg/g)	
Element	Before	After
Al	0.047 ± 0.007	2.53 ± 0.10
Ca	12.8 ± 0.2	11.4 ± 0.08
Fe	0.52 ± 0.14	0.17 ± 0.008
P	0.070 ± 0.006	0.051 ± 0.009
S	0.20 ± 0.027	6.60 ± 0.21

Performance of the alum-infused bark in removing dissolved phosphorus from water was evaluated under both laboratory and field conditions.

Time course phosphorus concentration at the inlet and outlet of the laboratory scale fitration unit is shown in Figure 5. Phosphorus concentration at the inlet was monitored only for the first 10 min, and at the outlet it was monitored for 48 min. At the flow rate of 8 L/min, phosphorus breakthrough volume was 176 L. At the breakthrough point, phosphorus concentration at the outlet was 2.7 ppm, compared with 4.5 ppm at the inlet. Thus, at the breakthrough point approximately 50% of the influent phosphorus was removed.

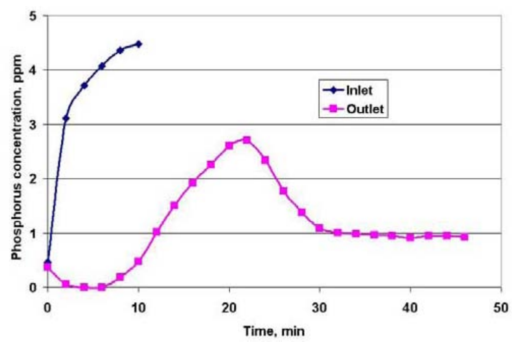

Figure 5 - Phosphorus concentrations at the inlet and outlet of the laboratory-scale filtration unit.

Field experiments

Time course phosphorus concentration at the inlet and outlet of the field scale filtration unit is shown in Figure 6, and the turbidity measured in NTU units is shown in Figure 7.

Although outlet and inlet phosphorus concentrations were not signficantly different, outlet and inlet turbidity values were measurably different. This highlights the effectiveness of the sorbent in removing suspended solids, which could be composed of phosphate-binding insoluble metal-humic or fulvic acid complexes. Periodic spikes in outlet phosphorus concentrations are indicative of periodic leaching of phosphorus caused by competitive binding of natural organic anions. The initial spike in phosphorus concentration at 20 min is a result of leaching of intrinsic phosphorus from the sorbent. Subsequent spikes at 120 and 220 min could result from leaching of bound phosphorus caused by competitive binding of natural organic anions for phosphorus binding sites on the sorbent. For example, natural humic or fulvic acid anions can compete for the same binding sites on the bark sorbent. Also, in addition to competitive binding of natural organic acids, the higher flow rate of the tail water (12 L/min) would be expected to adversely affect facile adsorption of orthophosphate ions, particularly at the low phosphorus concentrations observed in the field. Average phosphorus concentrations before and after installation of the filter unit are summarized in Table 2.

CONCLUSIONS

This research has demonstrated the feasibility of using alum-infused bark sorbents for dissolved phosphorus removal from water under controlled laboratory conditions. However, under uncontrolled field conditions, removal of dissolved phosphorus from tail water was not as effective as that observed under laboratory conditions. Although bark-based sorbents offer a viable alternative as lowcost sorbents for removal of phosphorus from water, further research is apparently needed to improve adsorption of low phosphorus concentrations in cranberry bog tail water. Because the alum-infused bark did not perform as well as we expected under field conditions, we have developed another bark-based sorbent infused with a lanthanum salt.

Laboratory evaluation of this sorbent suggests that this may be a better sorbent for orthophosphate removal from water [2].

H City Point Cranberries, LLP work crew, from left Jeff Itzen, Jeremy Duerr, Chris Weidman, Kyle Duerr

FUTURE RESEARCH

Research on more efficient bark-based phosphorus sorbents will continue. New research will focus on improvement of adsorption capacity and selectivity of bark-based filtration sorbents for other anions of environmental concern, such as nitrates, arsenates, and perchlorates.

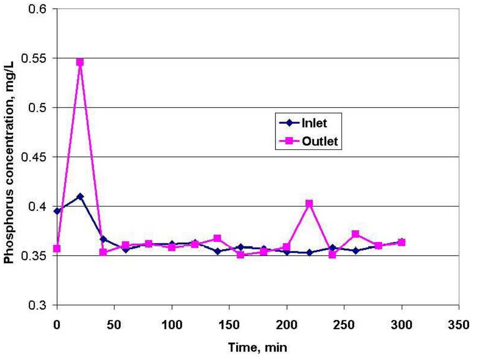

Figure 6 - phosphorus concentrations at the inlet and outlet of the field-scale filtration unit

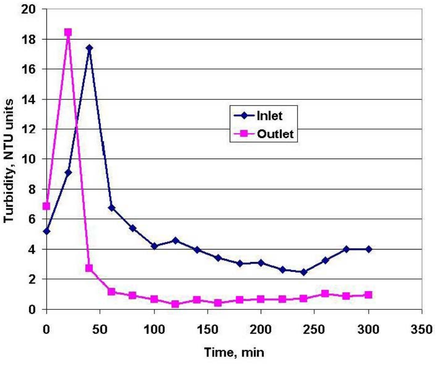

Figure 7 -Turbidity values of tail water at the inlet and outlet of the field-scale filtration

Sampling point	Phosphorus concentration (ppm)
Before installing unit	
Culvert inlet	0.39 ± 0.01
Culvert outlet	0.36 ± 0.03
After installing unit	
Culvert inlet	0.36 ± 0.01
Culvert outlet	0.37 ± 0.05

Table 2 - Comparison of average phosphorus concentration at culvert inlet and outlet

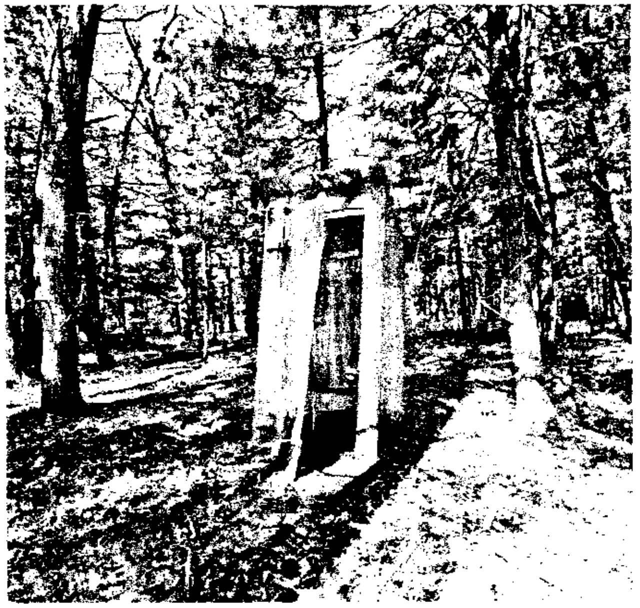
Photo by Dave Engel

H Outhouse stands among other debris that remain after fire destroyed original City Point Hunting Club shack in 1965. Many of the items damaged in the fire, such as the cookstove, remain on the site.

Citations

1. Tshabalala, Mandla A. (2003) "Use of Lignocellulosic Materials as Sorbents for Pesticide and Phosphate Residues." Wisconsin Cranberry Board Grant Final Report Supplement, February 2003 to October 2003.

2. EunWoo Shin, K.G. Karthikeyan, and Mandla A. Tshabalala (2005) "Orthophosphate Sorption onto Lanthanum-Treated Lignocellulosic Sorbents, Environ.Sci.Technol., Vol. 39(16);pp 6273-6279 ■

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August 9, 2006

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