USE OF MODIFIED PINE BARK FOR REMOVAL OF PESTICIDES FROM STORMWATER RUNOFF

Mandla A. Tshabalala
USDA Forest Service, Forest Products Laboratory
One Gifford Pinchot Drive, Madison, Wisconsin 53726-2398
Phone: 608-231-9505; Fax: 608-231-9262; email: mtshabalala@fs.fed.us

ABSTRACT

Pesticide entrainment in stormwater runoff can contribute to non-point source pollution of surface waters. Granular activated carbon has been successfully used for removing pesticides from wastewater. However, implementation of granular activated carbon sorption media in stormwater filtration systems comes with high initial capital investment and operating costs. Modified pine barks offer attractive alternative sorption media for use in stormwater filtration systems. Pine barks constitute a significant fraction of underutilized low-value waste materials from the forest products industry. The majority of the waste bark is used as a low-grade thermal fuel. We evaluated the effectiveness of modified pine bark for removing pesticides from water under dynamic conditions by percolating water solutions of pesticides through fixed bed columns of the test materials. We found that bark modified by grinding and treatment with an aqueous solution of N-methylpyrrolidinone (NMP), or with an NMP solution of stearic acid, or a methanol solution of sodium methylate is very effective in removing chlorpyrifos, chlorothalonil, and dichlobenil. Removal for chlorpyrifos was 88% to 96%; for chlorothalonil, 84% to 92%; and for dichlobenil, 39% to 90%. These results indicate that modified pine bark is as effective as granular activated carbon in removing hydrophobic pesticides from water and may be used as a less expensive alternative sorption medium for removal of pesticides from stormwater runoff.

KEYWORDS: pine bark, pesticide removal, sorption media, filtration, stormwater

INTRODUCTION

Along with municipal point sources and industrial discharges, urban stormwater runoff has been identified as a primary source of pollution of surface waters with pesticides [1]. Some pesticides, such as diazinon and chlorpyrifos, are commonly used in residential areas to control lawn and garden pests, including termites and ants. During a rainstorm or snowmelt event, residual pesticides are transported in runoff into the storm drain and ultimately accumulate in receiving streams, rivers, lakes, and estuaries, where they can harm aquatic organisms by killing them outright or by impairing their ability to grow or reproduce. In a recent study, Bailey et al. [2] determined levels of diazinon and chlorpyrifos in water samples collected from urban streams during the precipitation season and found higher levels of these pesticides in catchments receiving stormwater runoff from residential areas than from commercial and industrial areas.

A wide selection of best management practices (BMPs) are used to control stormwater runoff in urbanized areas. These include infiltration, flow attenuation, retention, detention, and extended detention. However, implementation and installation of these BMPs in existing urban areas can often be problematic because of limited space aboveground. Consequently, there is a growing interest in new retrofit BMP technologies, such as the multi-chambered treatment train (MCTT) that use underground space [3,4]. An MCTT is effective for removing sediment-bound pollutants and can also be designed to

Table 1. Use of bark as sorption media for water pollutants

Sorption medium	Application	Reference
Pine bark	Metals (Cd, Cu, Ni)	Al-Asheh and Duvnjak, 1998 [7]
Raw and chemically treated oak, pine, beech, and spruce bark	Non-metal (As) and metals (Cd, Cu, Zn, Cr, Pb, Fe, Hg, Ni)	Gaballah and Kilbertus, 1998 [8]
Modified spruce, pine, Douglas-fir, white larch, teak, and Afzelia bark	Metals (Cu, Pb, Ni, Fe, Cr)	Gloaguen and Morvan, 1997 [9]
Coniferous bark	Metals (Cd, Cu, Zn)	Seki et al., 1997 [10]
Teak wood bark	Dyes (Safranine and Methylene Blue)	Mackay et al., 1999 [11]
Eucalyptus bark	Reactive dyes (Remazol BB)	Morais et al., 1999 [12]
Pine bark	Pesticides (Organochlorines)	Bras et al., 1999 [13]
Pine bark	Pesticides (Metolachlor)	Grey et al., 1996 [14]
Cationized pine bark	Nutrients (Orthophosphate anions)	Tshabalala et al., 2003 [15]
Modified pine bark	Pesticides (Chlorpyrifos, chlorothalonil, dichlobenil)	Tshabalala, 2003 [this work]

remove a substantial amount of dissolved constituents of stormwater runoff. For example, by appropriate choice of filtration media, an MCTT can be designed to remove dissolved organic pollutants, including pesticide residues. One approach that has great potential for removing a wide range of dissolved pollutants is the use of mixed filtration media, consisting of sand, peat, and activated carbon. Sand has a high removal rate for suspended solids, and peat and activated carbon have high removal rates for dissolved pollutants. While peat and activated carbon are effective in that regard, they have some limitations. Peat may leach some nutrients such as phosphorus, depending on its origin and water chemistry [5], and in addition, it may not be readily available in some regions because of possible conflict with bog preservation [6]. Use of activated carbon comes with high initial capital and operating costs. Thus, a widely available and less-costly filtration medium is needed for treatment of urban stormwater runoff.

With growing concern over unsustainable use of global natural resources, including energy and water, there is renewed interest in the development of environmentally benign filtration materials. Table 1 lists a sampling of recent studies on the use of bark for removal of a variety of dissolved pollutants in water. Most of the uses are focused on removal of metal ions from water.

We are evaluating filtration media derived from bark for effectiveness in removing both sediment-bound and dissolved constituents of stormwater runoff. In this report we present preliminary results on the effectiveness of modified pine bark for removal of pesticides from water. Pine bark is widely available and is an underutilized, low-cost by-product of the forest products industry. The majority of bark is commonly used as low-grade thermal fuel to avoid solid waste management problems.

Pine bark is thick and porous and consists of extractable and nonextractable chemical components [16]. A significant fraction of the extractable components can be removed by extraction with hot water. The remaining nonextractable components, which consist of polysaccharides, phenolic polymers, and cross-linked polyesters, have the capacity to interact with a wide variety of solutes in water, including metal ions, and different classes of organic compounds. In the current study we used bark that consisted mainly of loblolly pine bark (*Pinus taeda* L). Physical properties of southern pine bark are summarized

Table 2. Physical properties of southern pine bark [17]

Species – location	Double bark thickness (cm)	Percentage bark by weight	Specific gravity	Calculated porosity, v_a
Loblolly – GA	0.46 – 4.2	8.8	0.303	0.64
Loblolly – SC	0.46 – 4.4	9.8	0.282	0.65
Slash – GA	0.97 – 4.9	12.7	0.341	0.61
Slash – SC	0.86 – 4.8	13.0	0.307	0.63

Note: $v_a = 1 - G(0.653 + 0.01\,M)$[18], where v_a is porosity, G specific gravity, and M moisture content.

in Table 2. Loblolly pine bark is quite porous, and its thickness varies from approximately 0.46 to 4.4 cm depending upon its location on the tree stem.

MATERIALS AND METHODS

Preparation of sorption media: Bark chips (Figure la), consisting mainly of loblolly pine, were obtained from a lumber mill in Louisiana. The bark chips were hand sorted to remove wood chips, and rinsed with running tap water to remove dirt. After air-drying, the bark chips were ground in a Wiley mill equipped with a 1-mm screen. The ground bark was sieved into fractions of different mesh sizes (>60, 60/80, 80/100, 100/200 mesh, and fines). One fraction (60180) mesh (Figure 1b) was selected for use in the current experiments. The other fractions were stored in a cold room to be used in other experiments.

Activation of ground bark: To remove extractives and activate the bark, ground bark was extracted in a Soxhlet apparatus for 24 h with a 10% aqueous solution of N-methylpyrrolidinone (NMP). The extracted ground bark was first air-dried and then placed in an oven at 105°C to drive off the remaining water and volatile extractives.

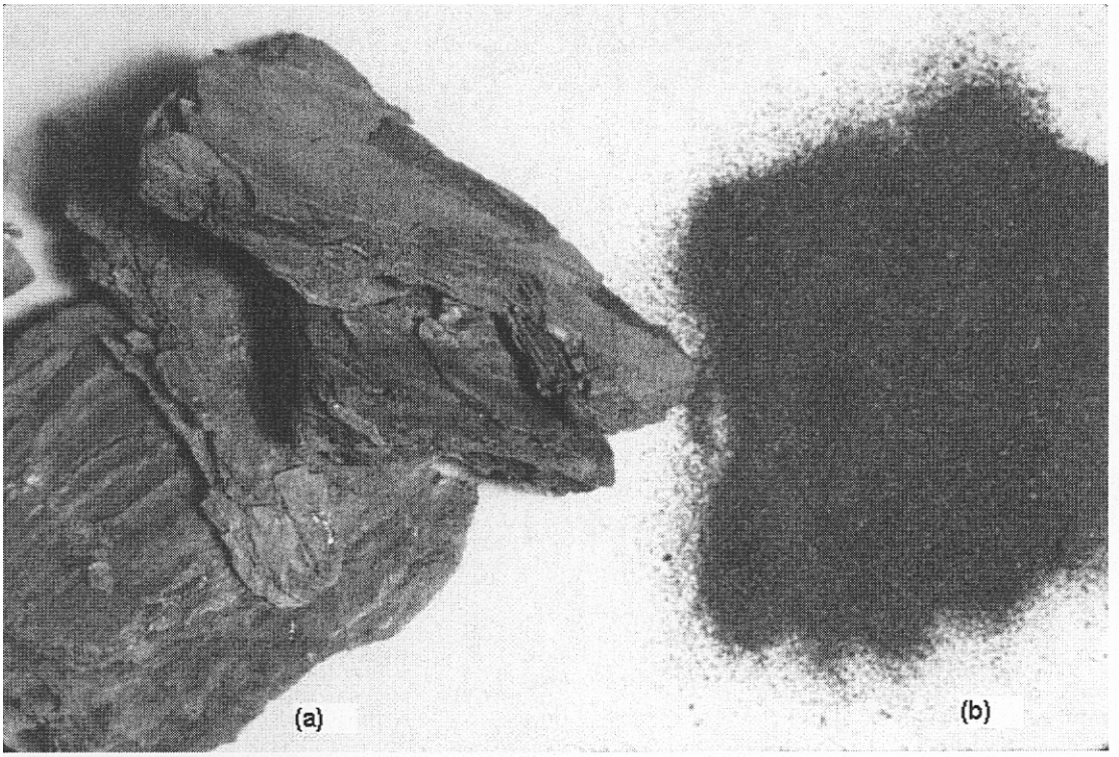

Figure I. (a) Loblolly bark chips and (b) 60/80 mesh ground bark

Table 3. Modification of surface chemistry of bark

Reagent	Treatment conditions	Purpose
10% aqueous solution of NMP	Soxhlet extractor, 24 h	Remove extractives
25% methanol solution of sodium methylate	Reflux for 3 h at 60°C	Modify hydrophilic character of bark by methanolysis
5% NMP solution of stearic acid	Heat for 15 min at 105°C in the presence of an acid catalyst	Modify hydrophilic character of bark by esterification

Surface chemistry modification: To modify the hydrophilic properties of the bark, activated samples of the ground bark were treated with methanol in the presence of a strong base or with stearic acid dissolved in NMP. The treatment conditions are summarized in Table 3.

Measurement of hydrophobicity: Changes in the hydrophobicity of bark sorbents due to chemical treatments were determined by vigorously mixing 0.5 g of each bark sample with a mixture of water and hexane in a 16- by 150-mm glass test tube and then allowing the mixture to equilibrate at room temperature for 1 h. Some of the sample partitioned into the water layer, and the rest partitioned into the hexane layer. To determine the weight of sample that partitioned into the hexane layer as a result of buoyancy, parallel determinations were made by vigorously mixing 0.5 g of each bark sample with water alone and measuring the weight of sample that partitioned to the air–waterinterface. All measurements were run in triplicate. The relative index of hydrophobicity Δ_{rel} was calculated from

$$\Delta_{rel} = W_{HX} - W_{AW}/W_W \quad (1)$$

where W_{HX}, W_{AW}, and W_W are the weights of samples partitioned into the hexane, air–waterinterface, and water layer, respectively.

Pesticide sorption experiments: A 2-g sample of the sorption material, weighed accurately to two decimal places, was placed in a 10.5- by 300-mm glass column equipped with a stopcock and allowed to equilibrate overnight under water. The column bed was rinsed with five column volumes of water before 500 mL of an aqueous solution of pesticides (chlorpyrifos, chlorothalonil, and dichlobenil) was percolated through the column bed under gravity flow. Flow rate was controlled by means of the stopcock and was kept at approximately 5 mL/min

Pesticide analysis in column effluent: The column effluent was concentrated by solid phase extraction on a C-18 cartridge. Pesticide concentration in the extract was determined by gas chromatography with mass selective detection (GC–MSD),using a 30-m DB5-MS capillary column equipped with a 5-m megabore capillary guard column.

RESULTS AND DISCUSSION

The extent of pesticide removal by different sorption media from water spiked with 100 ppb each of dichlobenil (DBN), chlorothalonil (CTL), and chlorpyrifos (CPS) is represented graphically in Figure 2. The extent of pesticide removal is expressed as percentage removal, and is calculated from

$$\text{Percentage removal} = 100(C_{in} - C_{out})/C_{in} \quad (2)$$

where C_{in} and C_{out} are the column influent and effluent concentrations of each pesticide.

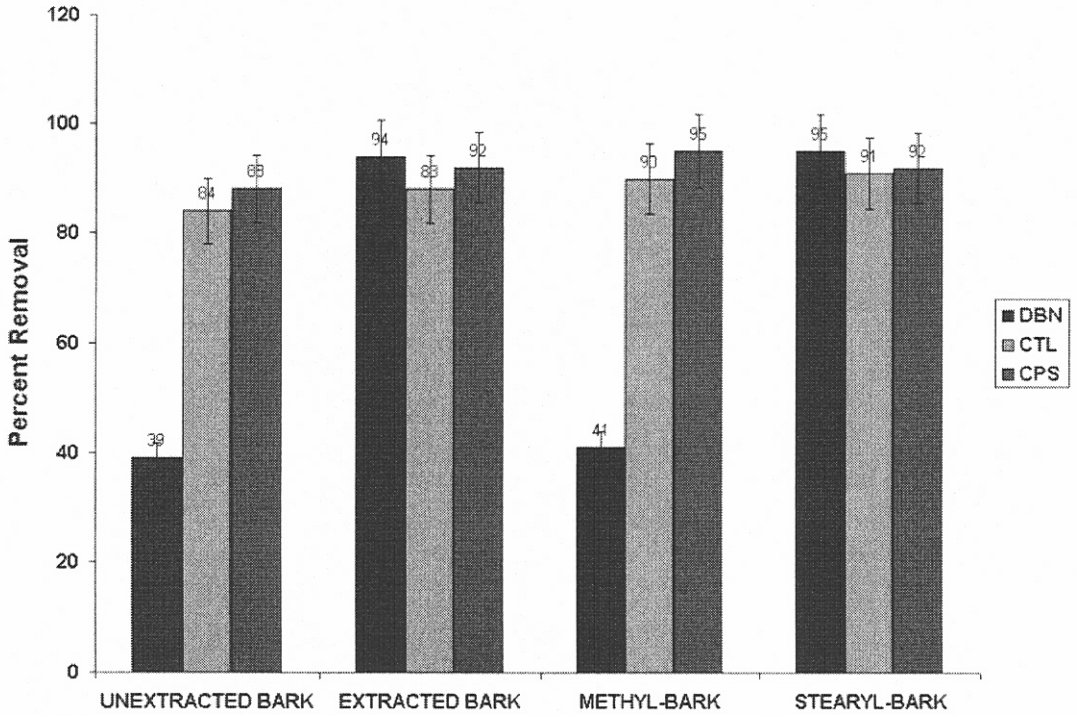

Figure 2. Percentage removal of dichlobenil, chlorothalonil, and chlorpyrifos from water by modified bark

Extracted bark and bark treated with stearic acid showed relatively high percentage removal for all three pesticides. Unextracted bark and bark treated with methanol solution of sodium methylate showed relatively low percentage removal for dichlobenil. Although the sorption mechanism of pesticides by bark is not yet fully understood, these preliminary results suggest that partitioning of pesticides from water to the bark is related to the hydrophobic properties of both the bark and the pesticides. We expected treatment of extracted bark with stearic acid to enhance its hydrophobic character. Stearic acid treatment appears to have led to an increase in the relative hydrophobicity of the bark (Figure 3). Use of stearic acid and its derivatives as a hydrophobic agent has been practiced for many years. The observed slight increase in percentage removal of all three pesticides by bark treated with stearic acid supports our hypothesis that hydrophobicity of the bark may have a strong influence on the partitioning of hydrophobic pesticides from water to the bark sorbent. On the other hand, the purpose of treating extracted bark with the methanol solution of sodium methylate was to depolymerize the polyesters that constitute bark tissue [19] and modify its surface chemistry. Apparently this treatment enhanced the selectivity of the bark for different pesticides. In particular, methylated bark appears to have a higher affinity for chlorpyrifos, which has a relatively high octanol–water coefficient (P_{ow}), than for dichlobenil, which has a lower P_{ow}.

The relationship between percentage removal and the logarithm of octanol–water coefficient (Log P_{ow}) is shown graphically in Figure 4. The following information can be drawn from these graphs:

- Stearic acid treatment modified the hydrophobic character of the extracted bark so that sorption of all three pesticides was so high as to be almost independent of their octanol–water coefficient.
- Methanol treatment in the presence of a strong base, sodium methylate, modified the selectivity of the bark for the pesticides. Sorption of the pesticides by methylated bark was strongly dependent on their octanol–water coefficient.
- Extracted bark and bark treated with stearic acid showed higher sorption affinity for all three pesticides compared with the type of granular activated carbon (GAC) used in this study. It was observed that this GAC was difficult to wet with water. Poor wetting characteristics may have resulted in less efficient transfer of the pesticides from the aqueous to the solid phase.

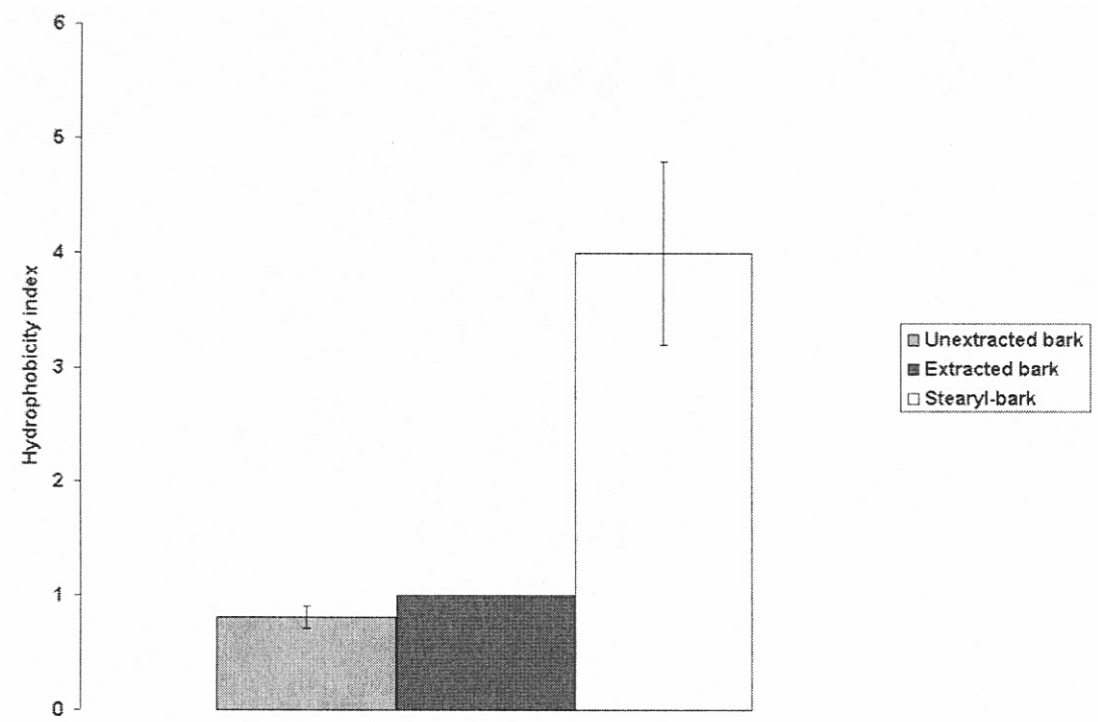

Figure 3. Comparison of hydrophobicity of samples of bark subjected to different modification schemes

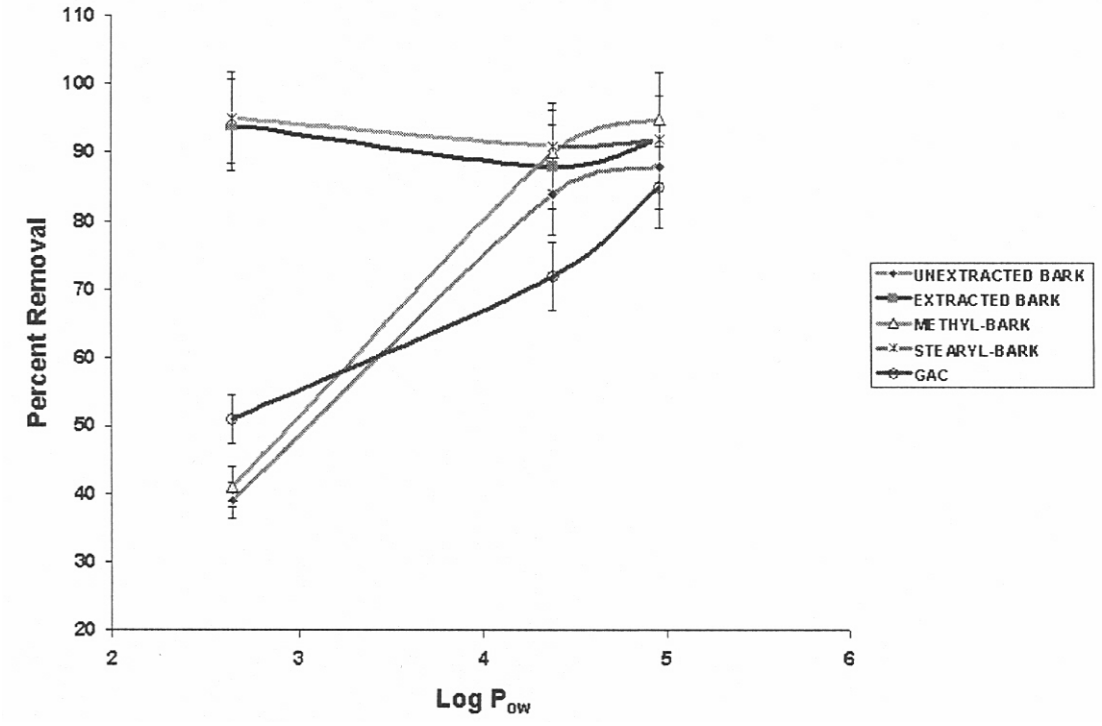

Figure 4. Plots of percentage removal from water versus Log P_{ow} of pesticides

CONCLUSIONS AND FUTURE WORK

We have demonstrated that modified pine bark has the potential for removing hydrophobic pesticides from water. These preliminary results suggest that pesticide sorption depends on the surface chemistry of bark and its hydrophobic characteristics and also on the chemistry of the pesticide. However, it is also

likely that the extent of pesticide sorption by bark will also be influenced by the particle size of the sorption media, which in turn determines the total surface area of the sorption bed that is available for interaction with pesticides in water. Hence, in addition to elucidating the mechanism of pesticide adsorption from water, future studies will also focus on the effect of particle size on percentage removal of pesticides from water. Such studies will allow us to determine the optimal particle size of bark sorption media that combines both high permeability to water flow and high sorption capacity for pesticides in water.

ACKNOWLEDGMENTS

USDA Forest Service Forest Products Laboratory, Massachusetts Department of Food and Agriculture, Cranberry Institute, Cape Cod Cranberry Growers Association, and Wisconsin Cranberry Board provided financial support for this project.

REFERENCES

1. United States Environment Protection Agency, Office of Water, Washington DC 20460. (2002) "National Water Quality Inventory: 2000 Report EPA-841-R-02-001."

2. Bailey, H.C., L. Deanovic, E. Reyes, T. Kimball, K. Larsson, K. Cortright, V. Connor, and D.E. Hinton. (2000) "Diazinon and chlorpyrifos in urban waterways in northern California, USA." Environ. Toxicol. Chem., Vol. 19(1); 82 – 87

3. Corsi, Steven R., Steven R. Greb, Roger T. Bannerman, and Robert E. Pitt. (1999) "Evaluation of the Multi-Chambered Treatment Train, a Retrofit Water-Quality Management Device." USGS Open-File Report 99 – 270

4. Pitt, R., B. Robertson, P. Barron, A. Ayyoubi, and S. Clark. (1999) "Stormwater Treatment At Critical Areas: The Multi-Chambered Treatment Train (MCTT)." EPA/600/R-99/017

5. Koerlsman, W., M.B. Van Kerkhoven, and J.T.A. Verhoeven (1993) "Release of inorganic N, P, and K in peat soils: effect of temperature, water chemistry and water level." Biogeochemistry 20: 63 – 81

6. Schmilewski, G.K. (1984) "Aspects of the raw material peat – resources and availability." Acta Hort. (ISHS) 150: 601 – 610

7. Al-Asheh, S., and Z. Duvnjak (1998) "Binary Metal Sorption by Pine Bark: Study of Equilibria and Mechanisms." Sep. Sci. Technol., 33(9); 1303 – 1329

8. Gaballah, I., and G. Kilbertus (1998) "Recovery of heavy metal ions through decontamination of synthetic solutions and industrial effluents using modified barks." Journal of Geochemical Exploration 62: 241 – 286

9. Gloaguen, V., and H. Morvan (1997) "Removal of heavy metal ions from aqueous solution by modified barks." J. Environ. Sci. Health A32 (4): 901 – 912

10. Seki, K., N. Saito, and M. Aoyama (1995) "Removal of heavy metal ions from solutions by coniferous barks." Wood Sci. Technol., 31: 441 – 447

11. Mackay, G., J.F. Porter, and G.R. Prasad (1999) "The removal of dye colours from aqueous solutions by adsorption on low-cost materials." Water, Air, and Soil Pollution 114: 423 – 438

12. Morais, L.C., O.M. Freitas, E.P. Gonçalves, L.T. Vasconcelos, and C.G. González Beça (1999) "Reactive dyes removal from wastewaters by adsorption on eucalyptus bark: variables that define the process." Wat. Res. Vol. 33(4): 979 – 988

13. Brás, I.P., L. Santos, and A. Alves (1999) "Organochlorine Pesticides Removal by Pinus Bark Sorption." Environ. Sci. Technol. 33: 631 – 634

14. Grey, T.L., G.R. Wehtje, B.F. Hajek, C.H. Gilliam, G.J. Keever, and P. Pace (1996) "Adsorption, Mobility, and Filtration of Metolachlor in Container Media." J. Amer. Soc. Hort. Sci. 121 (3): 478 – 482

15. Tshabalala, M.A., K.G. Karthikeyan, and D. Wang (2003) "Cationized Milled Pine Bark as an Adsorbent for Orthophosphate Anions." In press

16. Martin, R.E., (1969) "Characterization of Southern Pine Barks." Forest Products J. Vol. 19(8): 23 – 31

17. Phillips, D.R., and J.G. Schroeder (1972) "Some Physical Characteristics of Bark From Plantation-Grown Slash and Loblolly Pine." Forest Products J. Vol. 22(10): 30 – 33

18. Siau, J.F. (1995) in "Wood: Influence of moisture on physical properties," Department of Wood Science and Forest Products, Keene, New York, pp 13 – 17

19. Pereira, H. (1988) "Chemical composition and variability of cork from *Quercus suber L.*" Wood Sci. Technol. 22: 211 – 218

Storm Con [electronic resource]: The north American Surface Water Quality Conference & Exposition: July 28-31, 2003, San Antonio Texas. Santa Barbara, CA: Forester Communications, Inc., 2003: 8 p