The Society for engineering in agricultural, food, and biological systems

Paper Number: 025001
An ASAE Meeting Presentation

Use of Lignocellulose Materials as Sorption Media for Phosphorus Removal

K.G. Karthikeyan, Assistant Professor, Biological Systems Engineering, University of Wisconsin, 460 Henry Mall, Madison, WI 53706. kkarthikeyan@facstaff.wisc.edu

Mandla A. Tshabalala, USDA Forest Service Forest Products Laboratory, One Gifford Pinchot Drive, Madison WI 53705-2398. matshabalal@wisc.edu

Dongmei Wang, Grad. Student, Biological Systems Engineering, University of Wisconsin, 460 Henry Mall, Madison, WI 53706. dongmeiwang@students.wisc.edu

Written for presentation at the
2002 ASAE Annual International Meeting / CIGR XVth World Congress
Sponsored by ASAE and CIGR
Hyatt Regency Chicago
Chicago, Illinois, USA
July 28-July 31, 2002

Abstract. *The suitability of modified bark or wood fiber derived from southern yellow pine to function as P sorbents was investigated. Sorbent preparation process included grinding, size fractionation] extraction for surface activation] and treatment with polyallylamine hydrochloride (PAA·HCl) or 3-chloro-2-hydroxypropyltrimethlyammonium chloride. SEM images revealed surface morphology changes of these fibers due to extraction and chemical treatment. A greater than 200% increase in N content of PAA-bark compared to control (extracted bark) together with the appearance of a strong Cl peak in the EDXA spectra of the treated bark or wood provided evidence of attachment PAA·HCl to these fibers. Surface charge of PAA-treated bark was positive in the pH range 2.5 - 8, and turned negative at pH greater than 8. In contrast, the surface charge of untreated bark remained negative throughout the pH range, 2.5 - 9. Percent P removal decreased with increasing P concentration, with PAA-bark having a higher sorption capacity (11.96 mg P/g fiber) than PAA-wood (7.45 mg P/g fiber). Two distinct sorption regions, corresponding to high and low affinity sites, could be identified and the batch data were described using a multi-site Langmuir model. Both the sorption capacity and binding energy decreased with increasing ionic strength, due to competition for the available anion exchange sites. We propose that the mechanism for P sorption involves electrostatic attraction and/or specific interactions (between the surface functional groups containing -NH_2^+- and $H_2PO_4^-$/HPO_4^{2-}) and ion-exchange (between Ct and $H_2PO_4^-$/HPO_4^{2-}).*

Keywords. *lignocellulosic materials, bark, wood, phosphorus, sorption, ion-exchange.*

I. INTRODUCTION

By-products from agricultural and wood industries constitute the most abundant renewable resources available worldwide. Among these by-products, bark constitutes a significant portion of mill residues. For example, in 1996 approximately 24.5 million dry tons of bark residues were generated, of which 19.2 million tons were used as fuel, 4.53 million tons in miscellaneous by-products, 0.117 million tons in fiber by-products, and 0.638 million tons were not used (USDA Forest Service, 1997). Bark could be an important renewable source of raw material for the chemical industry, but its widespread use is still hindered by lack of adequate technologies for separating its components into pure chemical fractions. Hence, bark is predominantly used as a low-grade thermal fuel or as landscaping mulch. Recently, there has been renewed interest in developing environmentally friendly products from bark including panel boards (Forestry Chronicle, 1998); polyphenols and adhesives (Adhesives & Sealants Industry, 2001); water-repellent formulations for wood products (Passialis et al, 1 999); and biodegradable polyurethane foams (Ge, 2000). In addition, our preliminary studies indicate that low value underutilized materials that are removed from the forest to reduce fuel loads can be converted to sorption media for removal of pesticides and toxic heavy metals from wastewaters.

Water quality issues are of paramount concern and recent data indicate that 90% of the people in the United States are living within 10 miles of a body of contaminated water (Hogue 2000). Since the promulgation of the Water Pollution Control Act Amendments in 1972, hundreds of billions of dollars have been spent to cleanup pollution caused by municipal and industrial wastewater. Despite these enormous cleanup efforts, pollution from land areas of intensive agriculture and urban use [i.e., non-point pollution] has continued to impair the quality of water bodies (Novotny and Olem, 1994). The United States Environmental Protection Agency [USEPA] is working on guidelines and regulations to establish total maximum daily load [TMDL] for each pollutant that is of concern in a particular watershed (Hogue, 2000). The materials listed by USEPA include sediments, nutrient [phosphorus (P) and nitrogen (N)], metals, pesticides, dissolved oxygen, suspended soils, and turbidity.

Discharges from numerous point and non-point sources [e.g., agricultural, urban runoff, municipal wastewater treatment, industrial, mining activities] have resulted in excessive levels of contaminants in the environment. Implementation of tighter controls for point sources has forced the municipalities/industries to successfully adopt the well-known chemical and biological treatment methods. Therefore, the focus has now shifted to non-point sources (Moore and Miller, 1994), for which cost-effectiveness of treatment, besides removal efficiency, will determine its ultimate applicability. Agricultural inputs of P and N are major contributors of non-point source pollution to surface water bodies (Pote et al., 1996). The diffuse nature and the scale of non-point sources prohibit extensive application of the above processes to treat agricultural runoff. The installation costs can be as high as $3 million/site, and the annual maintenance costs can be as high as $30,000 (Roger Bannerman, Wisconsin Department of Natural Resources [WDNR] - personal communication). Therefore, there is an urgent need to develop cost-effective alternate treatment technologies for large-scale removal of nutrients, pesticides and toxic heavy metals from agricultural and urban runoff. The major goal of this study is to develop treatment technologies for converting low value and underutilized forest residues, which are composed of up to 30% by volume of bark, to low-cost and efficient sorbents for minimizing nutrient levels in runoff from cattle feedlots, agricultural lands, and other similar non-point sources of water pollutants. Specific objectives are to: (i) tailor the surface properties of bark or wood to enhance their sorption capacity for anions, (ii) characterize the surface properties of modified lignocellulosic fibers, and (iii) quantify the P sorption capacity and elucidate the mechanisms of interaction.

II. BACKGROUND

Various sorbent systems based on mineral and plant materials have been proposed in the literature. These natural materials exhibit a high affinity for cationic metals (Gloaguen and Morvan, 1997; Bailey et al., 1999). For example, the maximum Pb sorption capacity of bark, chitosan, lignin, seaweed, and zeolite is 182 mg/g (Teles de Vasconcelos and Gonzalez Beca, 1994), 796 mg/g (Masri et al., 1974), 1587 mg/g (Srivastava et al., 1994), 344 mg/g (Leusch et al., 1995) and 155 mg/g (Leppert, 1990), respectively. A number of researchers have evaluated the capacity of lignocellulose materials for removing organic contaminants, such as, pesticides, oils, and reactive dyes from industrial processes or wastewater streams. McKay et al. (1999) showed that teak wood bark, rice husk, and cotton waste have a high adsorption capacity for Safranine and Methylene Blue dyes in aqueous solution. Edgehill et al. (1998) evaluated the adsorption characteristics of carbonized bark from slash pine for phenol and pentachlorophenol. Bras et al. (1999) showed that the removal efficiency of pine bark for organochlorine pesticides in water ranged from 38% to 97%. Krishnan et al. (1998) demonstrated the use of percolating columns charged with layers of gravel, soil, sawdust and bark for treatment of wastewater from maize processing industry. Morais et al. (1999) investigated the adsorption capacity of eucalyptus bark for removing reactive dyes from wastewater. Martin-Gullon and Font (2001) reported that pelletized pitch-based activated carbon fibers have high removal efficiency for atrazine in water. Laszlo and Dintzis, (1994) observed that soybean hull and sugar beet fiber, treated with epichlorohydrin exhibited enhanced cation exchange capacity.

Although much progress has been made in developing low-cost sorbents for heavy metals and organic contaminants, applications focusing on removal of anionic species are rare. Phosphorus tends to occur as orthophosphates [$H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}], polyphosphates [polymers of phosphoric acid] and organically bound phosphates. A recent study has highlighted the potential of synthetic crosslinked polymeric hydrogel to remove P from aquaculture wastewater effluents to low enough levels [< 0.01 mg/L] as to facilitate direct discharge to natural surface waters (Kioussis et al., 1999). This sorbent was synthesized by crosslinking poly(allylamine hydrochloride) [PAA □ HCl] with epichlorohydrin in aqueous solution to form a water-insoluble polymer network with fixed ammonium sites for anion exchange with phosphate anions in solution. These initial results are promising and extensions to lignocellulose-based hydrogels appear logical.

Bark has a number of attributes that make it attractive as a sorbent material. Bark is abundant, inexpensive and is a by-product of the timber processing industry. Bark is insoluble in water, highly porous and contains polyphenols and lignin in addition to polysaccharides (Martin, 1969; Nickles and Rowe, 1962; McGinnis and Parikh, 1975). The hydroxy groups on the polyphenols provide natural cation exchange sites. The hydroxy groups on the polyphenols, lignin and polysaccharides can also be used to attach alkoxyamine ligands to afford bark anion exchange properties. The highly developed porous structure of bark allows it to absorb large amounts of water but still remain insoluble very much like a synthetic hydrogel.

Deterioration of water quality of streams and lakes in the United States and worldwide through non-point sources [NPS] of pollution is a growing environmental concern (Sharpley et al., 1999). A major contributor to non-point sources of P and N to surface water bodies is agriculture (Sharpley et al., 1994; Pote et al., 1996). Phosphorus and N are naturally occurring elements that are essential for crop and animal production. Despite posing no known direct toxic risks for humans or animals, environmental concern with P and N are due to their ability to accelerate biological productivity [i.e., eutrophication] of surface waters. Eutrophication is associated with incidence of algal blooms, which may be toxic to livestock and humans, increased water treatment costs, depleted oxygen levels in the water, increased incidence of

fish kills, and decreased perceived aesthetic value of water bodies (Sharpley et al., 1994; Daniel et al., 1994; Daniel et al., 1998; Carpenter et al., 1998; Sharpley et al., 1996; Sharpley et al., 1998). While N is a major cause of eutrophication of coastal ecosystems, many lakes are most directly affected by P inputs (Schindler, 1977). Non-point inputs of P cause eutrophication of a large number of freshwater water-bodies in the United States (U.S. EPA, 1990, 1996; NRC, 1992; Carpenter et al., 1998). Over the past few years, the focus has shifted to P due to imbalances occurring in P inputs and outputs, a direct consequence of rapid growth and concentration of livestock industry and commonly followed N-based manure management practices. Several management practices have been recommended to minimize contributions from agricultural field to non-point source pollution. Examples include conservation practices such as grassed buffer strips, field borders, reduced tillage, and improved irrigation and drainage management. Physical barriers such as vegetative filter strips have been examined for their ability to filter sediments and nutrients from runoff. These barriers are ineffective under conditions where concentrated flow occurs. With increased sediment accumulation, they tend to serve more like a terrace than a filter and there is a potential for nutrient release from trapped sediments (Dillaha et al., 1989). In addition, mechanisms involved in partitioning of nutrients in the filter strips are not clear and their long-term effectiveness is questionable. Conservation tillage approaches such as chisel plow and no-till systems are capable of minimizing erosion, and thereby the total P [TP] loads; however, these practices are ineffective in controlling dissolved P [DP, bio-available form with the maximum pollution potential] losses.

III. MATERIALS and METHODS

3.1 Preparation of Lignocellulosic Sorbents:

Wood or bark fibers of southern yellow pine were used to prepare P sorbents. The processes involved in sorbent preparation included grinding, size fractionation, extraction and chemical modification. Fibers were ground using a Wiley Mill and separated with stacked sieves into five size fractions: Fraction I: > 250 µm; Fraction II: 60/80 mesh (200 - 250 µm); Fraction Ill: 80/100 mesh (149 ~ 200 µm); Fraction IV: 100/200 mesh (149 ~ 74 µm); and Fraction V: Fines (< 74 µm). Fraction II (60/80 mesh) was selected for extraction as well as further chemical modification due to higher product recovery (compared to other smaller sized fractions) and uniformity in particle size (compared to fraction I). A biodegradable and easily recoverable organic solvent, 1:9 v/v 1 -methyl-2-pyrolidinone (NMP), was used for extraction to activate the surface of the fibers for subsequent chemical modification. Extraction is expected to increase the surface energy of the fibers thereby facilitating binding with reactive reagents. A thimble with 10 g of 60/80 mesh fiber was weighed and covered with a piece of cloth and then placed in a Soxhlet apparatus. The Soxhlet apparatus was then connected tightly to the top of an extraction round bottom flask containing 300 mL of 1:9 v/v NMP/H_2O. Six Soxhlet apparatus in parallel were used for one batch to extract for 24 hours. At the end of 24 hours, the Soxhlet apparatus were allowed to cool down and the thimble was removed. Then the thimbles were air-dried in a ventilation hood overnight, and dried in an oven at approximately 105°C for 6.5 hours. The thimbles were cooled to room temperature, removed from the oven, and weighed to determine the weight loss.

The extracted fibers were treated according to the surface chemistry modification schemes outlined below:

Scheme I: The extracted fibers were reacted with 1% PAA□HCl at a solid-to-solution ratio of 1:10 in a beaker using a magnetic stirrer for 20 min at room temperature. One mL of 6.25 M NaOH was added to this mixture and mixing was continued for another 20 min. One mL

epichlorohydrin was then added and the suspension was mixed vigorously for another 20 min. The mixture was then poured into a pan, air-dried overnight in a ventilation hood, and then placed in an oven to dry at approximately 105°C for 6.5 h. The chemically modified fibers were then cooled down to room temperature and weighed.

Scheme II: The extracted fibers were reacted with 4.375 M NaOH at a solid-to-solution ratio of 1:1.5 using a magnetic stirrer for 20 min at room temperature. Fifteen mL of 60% 3-chloro-2-hydroxypropyltrimethlyammonium chloride (CHPTMAC) was added and mixed vigorously for another 20 min. The mixture was then transferred to a funnel lined with No. 42 Whatman filter paper and filtered under vacuum. The filter cake was then washed with distilled water until the pH of the filtrate was close to 7, air-dried overnight and placed in an oven for drying at approximately 105°C for 6.5 h.

3.2 Physico-chemical Characterization of the Sorbents:

To investigate the changes in surface chemistry and morphology due to extraction and chemical modification, the following analyses were conducted on un-extracted, extracted, and modified wood and bark fibers: scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDXA), inverse gas chromatography (IGC), elemental composition and surface charge characterization. SEM analysis was performed using a JEOL 840 instrument at the USDA FPL, Madison WI. Percent C, H, and N content were determined using a CHN analyzer by Galbraith Laboratories, Inc. Knoxville TN. HP 5890 gas chromatograph with a 5970 mass selective detector interfaced to a HP chemstation was used in IGC experiments. PAA modified bark was weighed and packed in a glass column 1.2 m long and 4 mm internal diameter. The column was then equilibrated at 105°C for 1 week and transferred to HPGC. Experiments were performed at temperatures ranging from 50 to 100°C. Helium was used as a carrier gas. Saturated n-alkanes were used as neutral probes, carbon tetrachloride, chloroform and dichloromethane as acidic probes, and ether, tetrahydrofuran and ethlyacetate as basic probes. The retention time of each probe and the Ar(g) marker were determined using the HP chemstation. Zeta potential and electrophoretic mobility of PAA bark and extracted bark were measured using a Zeta Sizer 3000HS. The fibers were ground and sieved through a 270 mesh ($\approx$50 µm) sieve. Fifty mg of the sample was suspended in 100 mL MilliQ grade deionized (DI) water. Suspension pH was adjusted to be between 2 and 10 using either 0.01 M NaOH or 0.01 M HCl. After pH adjustment, the suspensions were equilibrated on a platform shaker for 24 hours. The suspensions were then allowed to settle for 1 h prior to zeta potential measurement.

3.3 Phosphate Batch Sorption Experiments:

Batch experiments were conducted in duplicates by adding 0.1 g of modified fibers to a 60 ml polypropylene (PP) bottle. Varying amounts of stock solution containing 1000 mg P/L were added to the PP bottle give a series of solutions with the following final P concentrations: 0.1, 0.5, 1, 2, 5, 10, 50, 100, 200, and 500 mg P/L. The total weight of fiber and solution in each bottle was adjusted to be equal to 40 g using DI water to provide a solid-to-liquid ratio of 1:400. The fibers were allowed to react with P solutions for 24 h at 25±1°C on a mechanical end-over-end shaker at 7 rpm. Fiber (without P) and P (no fibers and P) blanks were identically prepared. After equilibration, the suspensions were allowed to settle for 1 hour and then filtered through a 0.2 µm PP syringe filter. pH value of the filtrate was measured using an Accumet AR-50 pH/conductivity meter. The undigested filtrate was analyzed for dissolved reactive phosphate (DRP) using a Lachat autoanalyzer (Zellweger Analytics, Milwaukee, WI) by following the standard molybdate-based colorimetric methods at a wavelength of 880 nm (APHA, 1992). The difference between initial and final DRP concentrations was used to calculate percentage removal. The filtrate was also digested in a block digester using acid persulfate to determine

total dissolved P (TDP) (APHA, 1992). In addition, Cl, Ca and Fe remaining in solution after reaction of P with the sorbents were also determined. Chloride ion was measured using a DIONEX DX 500 ion chromatograph, and Ca and Fe were measured using a GBC 932 flame AA spectrophotometer.

The above-mentioned experiments were conducted in the absence of a background electrolyte (i.e., zero background). Subsequently, experiments were performed to determine the effect of solution chemistry (ionic strength, / and pH) on P sorption. Two different concentrations (0.01 M and 0.001 M) of NaCl were used to create different ionic strength values. A stock solution containing 1000 mg P/L in 0.01 or 0.001 M NaCl was diluted to obtain the desired initial P concentrations. To determine the effect of pH, 1.0 M NaOH solution was used in the above system to obtain final suspension pH values ranging from 3.5 to 8. DI water and 0.01 M NaCl were used as background electrolytes in the pH-effect experiments.

Sorption isotherms were constructed by plotting equilibrium DRP concentration (mg P/L) against sorption density (mg P sorbed/g fiber). Experimental data were modeled using the Langmuir and Freundlich equations. The linearized Langmuir adsorption equation is given as:

$$\frac{C_e}{q_e} = \frac{1}{k\, q_{max}} + \frac{C_e}{q_{max}} \qquad (1)$$

where, q_e is the amount of P sorbed [mg P/kg fiber], C_e is the solution concentration [DRP] after 24 h equilibration [mg P/L], q_{max} is the P sorption maximum (or) capacity [mg P/kg fiber], and k is a constant related to the energy of adsorption [L/ mg P]. A linear plot of the above equation yields the values of q_{max} and *k* (Snoeyink, 1990). The linearized Freundlich equation has the following form:

$$\log q_e = \log K + n \log C_e \qquad (2)$$

where, K [mg P/kg fiber] and *n* [L/kg] are constants. The adsorption constant [K] is related primarily to the capacity of the modified lignocellulose materials for P, and n is a function of the strength of adsorption.

IV. RESULTS and DISCUSSION

The extracted wood fiber is a polymer composite of polysaccharides and lignin, and the extracted bark is a polymer composite of polysaccharides, lignin and non-extractable polyphenols. All of these polymers contain reactive hydroxyl groups that can be used to attach alkylammonium functional groups on the fiber surface. Treatment with alkoxyamines is expected to reverse the fiber surface charge from negative to predominantly positive. Reaction of fibers with PAA·HCl is hypothesized to occur via the pathway shown in Figure 1, which provides a simplified schematic showing the attachment of a single PAA molecule to the lignocellulosic fibers. The ultimate product of the reaction is believed to be a complex network containing several sites substituted with the $-NH_3^+Cl^-$ functional groups, resulting in a dense population of cationic sites.

4.1 Physico-chemical Characterization of Lignocellulosic Sorbents:

SEM images revealed that extraction with NMP dissolved the matrix (lignin, hemicelluloses), exposed the microfibrils and resulted in the development of a porous surface with coarse fibrous texture making the surface more amenable for the attachment of reactive functional groups. Extraction ruffled the bark fiber surface tissue more extensively than the wood fiber. After PAA addition, the presence of ordered string-shaped surface structures and fine particle deposits were observed. The string shaped regions could correspond to the edge

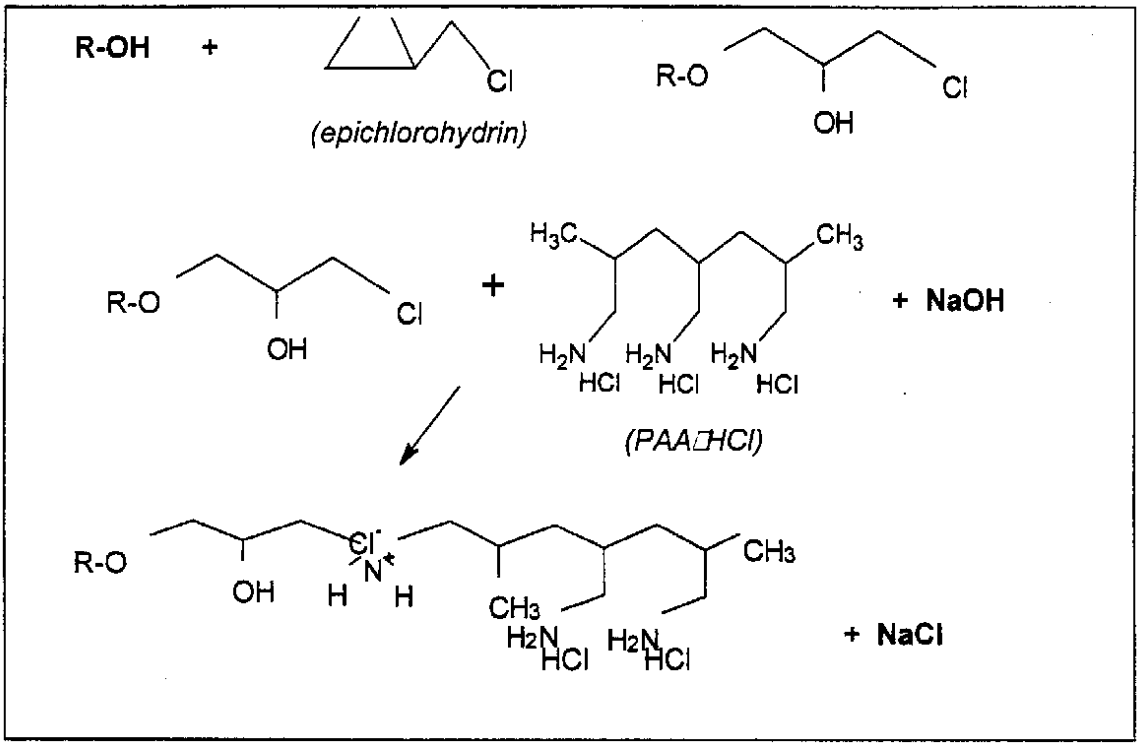

Figure 1. Schematic representation of reaction between lignocellulosic fibers and PAA□HCl (R represents a carbohydrate chain).

of a cell curvature containing a high density of PAA accumulation. Further evidence for PAA attachment and the cationized reaction scheme proposed in Fig. 1 was provided by EDXA results. Significant amount of Cl and a small peak for Na were observed only in the EDXA spectra of modified fibers. In addition, elemental composition data indicated a significant increase in N and Cl content of bark fibers subjected to PAA□HCl treatment, which supports our hypothesis that PAA is chemically bonded to the fiber surface via the hydroxyl groups on the polysaccharides, lignin or non-extractable polyphenols.

Figure 2 shows the variation in zeta potential of PAA-bark and the extracted bark fiber (control) ,as a function of suspension pH. The point of zero charge (pH_{ZPC}); defined as the pH at which the surface charge is zero, is around pH 7.9 for PAA-bark. Extracted bark fiber has a negative zeta potential, corresponding to its surface charge, between pH 2.5 to 9. The charge properties of PAA-bark and extracted bark are very different throughout the pH range used. It is, therefore, clear that the surface chemistry of extracted bark has been modified by the attachment of PAA polymeric chain, resulting in the development of a positive charge. At pH < pH_{ZPC}, surface of PAA-bark is positively charged. As a consequence, coulombic attraction can readily take place, in conjunction with specific chemical adsorption, between the anions (HPO_4^{2-} and $H_2PO_4^-$ and the adsorbent (PAA-bark). At pH > pH_{ZPC}, the surface is negatively charged, due to adsorption of OH- and/or deprotonation of the –NH3+-functional group ($-NH_3^+- \rightarrow -NH_2- + H^+$). Compared to other inorganic P sorbents, such as, SiO_2, ZnO_2, SnO_2, lanthanum-impregnated silica gel and aluminosilicates, PAA-bark has a higher pH_{ZPC}. This property will help extend its applicability as a P sorbent over a wide range of solution conditions.

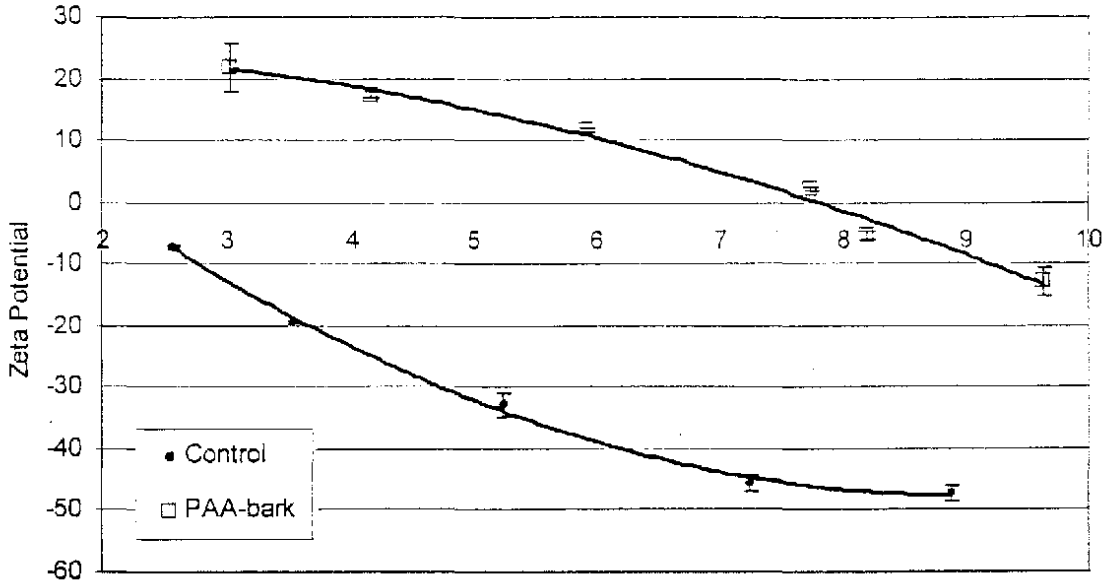

Figure 2. Surface charge characteristics of PAA-bark and extracted bark (control).

4.2 Phosphorus Sorption Experiments:

Percent P removal as a function of initial P concentration (C_o), ranging from 0 to 100 mg P/L, is shown in Figure 3. While PAA-bark and PAA-wood are effective in sorbing P, CHPTMAC modified bark removed only negligible amounts from solution. Percent P removal by PAA-bark and PAA-wood decreased with increasing C_o. At low initial P level (C_o < 10 mg P/L), greater than 80% removal could be obtained with both PAA-bark and PAA-wood. PAA-bark exhibited a slightly greater affinity towards P than PAA-wood, which is probably due to the extent of PAA attachment onto the fibers. This observation is supported by the results from SEM and EDXA analyses. SEM images clearly revealed the presence of string-shaped regions (due to PAA attachment) in modified bark and this effect was less pronounced in the case of PAA wood. Also, a larger CI peak could be observed in the EDXA spectrum of PAA-bark as compared to that for PAA-wood.

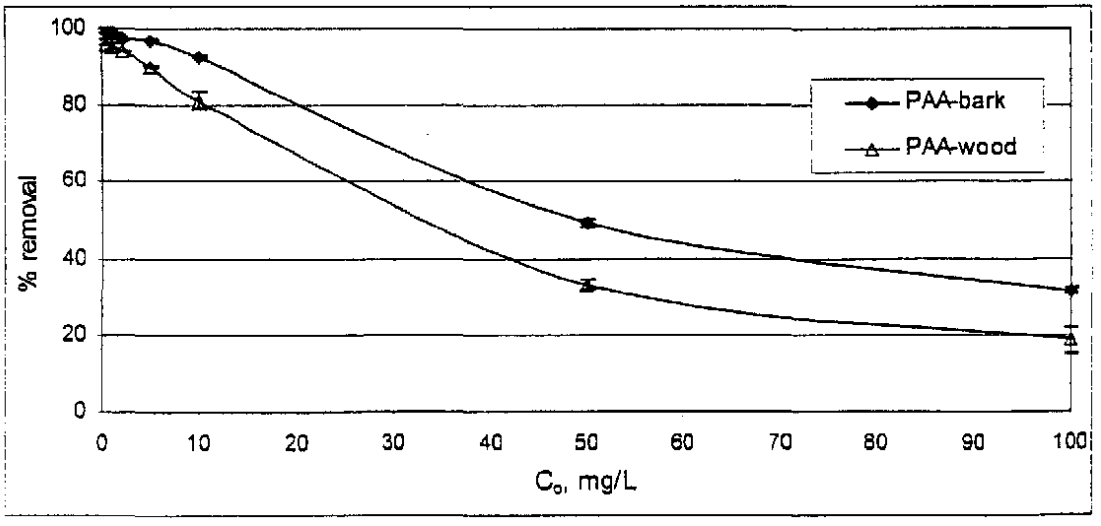

Figure 3. Phosphorus removal by PAA-bark and PAA-wood.

Our initial modeling efforts to describe the batch experimental data focused on the use of Langmuir (equn. 1) and Freundlich (equn. 2) models. If adsorption of P to PAA-bark conforms to the Langmuir model, a plot of equation (1) should result in a straight line with a slope $1/kq_{max}$ and intercept $1/q_{max}$. Data fitting of our experimental data to the Langmuir equation is shown in Figure 4a. Although the Langmuir model provided a good "overall" fit of the experimental data (r^2 of 0.9814 and 0.9948 for the isotherms for PAA-bark and PAA-wood, respectively), deviation from linearity (lower r^2 values, 0.94 and 0.97 for PAA-bark and PAA-wood, respectively) was observed at higher equilibrium P (C_e) levels (Figure 4b), specifically at C_e greater than 1.87 and 0.73 mg P/L for PAA-wood and PAA-bark, respectively.

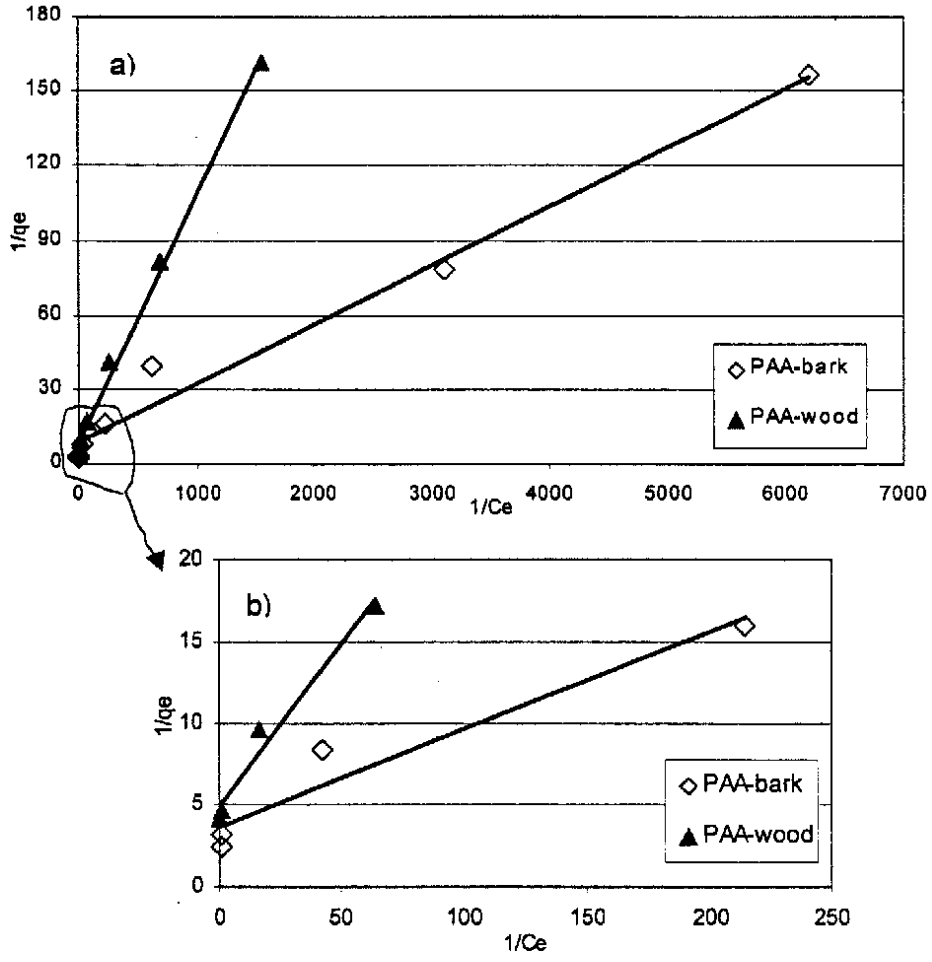

Figure 4. Fit of experimental data to the Langmuir model (a) entire C_e range; (b) low $1/C_e$ values.

Figure 5 illustrates the application of Freundlich model to describe P sorption onto PAA-bark and PAA-wood. Although a single straight line resulted a reasonable fit (r^2 = 0.96 and 0.94 for the isotherms for PAA-bark and PAA-wood, respectively), it is apparent that two sorption regions with different slopes (as a function of C_e) exist. These regions correspond to sites with different binding affinities. The hypothesis is that sorption initially takes place at the higher affinity sites and once these sites are saturated, further sorption occurs at the lower affinity sites. Similar observations have been reported for P adsorption to soils by Syers et al. (1973). Therefore, a multi-site model was applied to explain the sorption data.

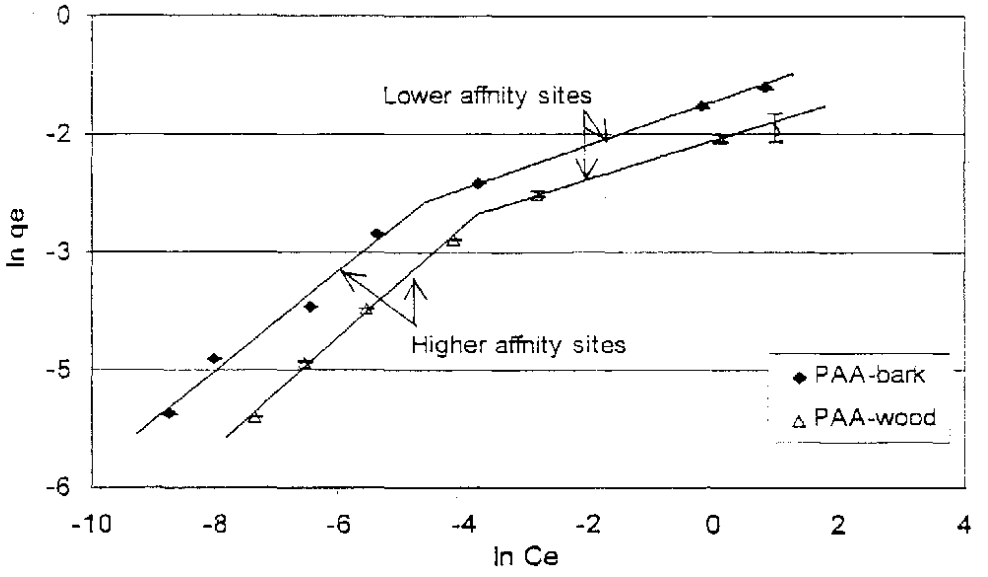

Figure 5. Description of P sorption by PAA-bark and PAA-wood using Freundlich equation.

The multi-site (2-sites) Langmuir equation can be expressed as (Bohn et al. 1985):

$$q_e = b_1 - \frac{q_e}{K_1 C_e} + b_2 - \frac{q_e}{K_2 C_e} \quad (3)$$

where the subscripts 1 and 2 refer to regions (or mechanisms) 1 and 2 containing sorption sites with different affinities (i.e., high and low), *K* and *b* are related to binding energy (strength) and maximum sorption capacity, respectively. The adsorption maximum for a sorbent *(b)* is the sum of b_1 (higher energy) and b_2 (lower energy). The multi-site model satisfactorily explained the data over the entire range of C_e values and the corresponding parameter values for different solution conditions are listed in Table 1. Although the adsorption maximum for the higher affinity sites (b_1) is almost the same for PAA-bark and PAA-wood, PAA-bark has sites with much higher binding energy (K_1 = 15.32 L/mg fiber) than those in PAA-wood (3.51 L/mng fiber). In addition, PAA-bark contains a much higher density of lower affinity sites than PAA-wood, resulting in a higher overall sorption capacity *(b).*

Table 1. Multi-site Langmuir model parameters for P sorption to PAA-bark and PAA-wood.

Samples	Region I		Region II		Overall	
	b_1 mg/g	K_1 L/mg	b_2 mg/g	K_2 L/mg	b^* mg/g	K^* L/mg
PAA-bark, DI	2.59	15.32	9.37	0.58	11.96	15.9
PAA-bark, 0.01M NaCl	2.40	0.68	5.22	0.09	7.62	0.77
PAA-wood, DI	2.78	3.51	4.67	0.41	7.45	3.92

($^*b = b_1+b_2$; $K = K_1+K_2$)

4.2.7 Effect of Solution Chemistry on P removal

Influence of ionic strength *(I)* and pH on P sorption by PAA-bark was investigated to determine solution chemistry effects. Two different I values, 0.001 M and 0.01 M NaCl were used and the results were compared with those obtained from experiments conducted in a DI water (zero background) medium (shown in Fig. 3). Figure 6 illustrates the effect of *I* on P sorption by PAA-bark. Competitive effects due to increasing *I* on P removal can be observed up to a C_o of 200 mg P/L, above which the difference is negligible. There are two possible ways by which *I* can influence P sorption onto PAA-bark: increasing *I* (i) decreases the solution-phase activity of $H_2PO_4^-$ and HPO_4^{2-} and (ii) increases concentration of competing anion (Cl^-). The activity coefficient effect is not significant, since $\{H_2PO_4^-\}$ decreases only by 10% when I increases from zero to 0.01 M (Snoeyink and Jenkins, 1980). Hayes et al., (1987) investigated ionic strength effect on anion adsorption onto oxides, and concluded that for anions strongly bonded to oxides (inner sphere complexion), changing the ionic strength (0.001 ~ 1 .OM) has little effect on the amount adsorbed. In the case of weakly bonded anions, the amount adsorbed is markedly reduced in the presence of competing ions. With increasing *I,* there is disproportional decrease in P removal (Fig. 6), which can be attributed to the presence of sorption sites with different affinitiesrk. While the density of strong sites *(b_1)* is not affected by the increase in *I,* the amount of P sorbed onto weak sites *(b_2)* is reduced 1.8 times due to competition from Cl^- (Table 1).

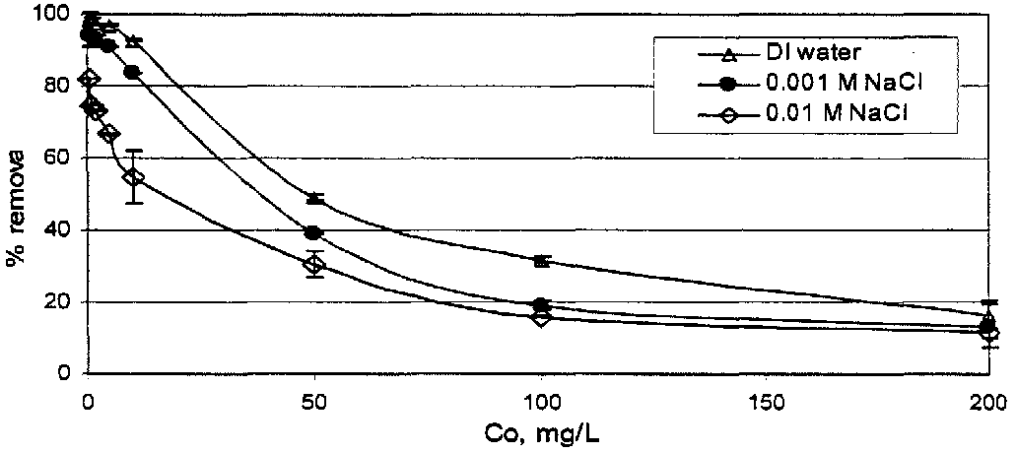

Figure 6. Effect of ionic strength on phosphate removal by PAA-bark.

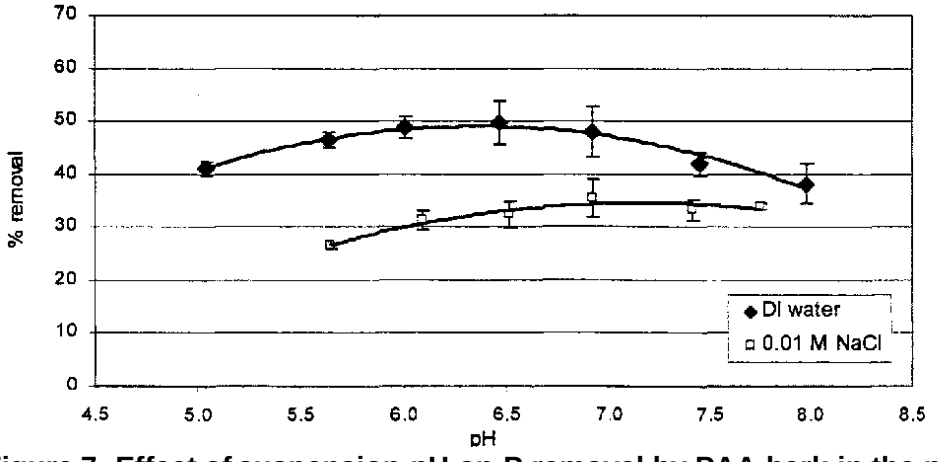

Figure 7. Effect of suspension pH on P removal by PAA-bark in the presence of DI water (zero background) and 0.01 M NaCl.

Effect of pH on P adsorption on PAA-bark was investigated by adjusting suspension pH to be in the range of 3 - 8 using 0.01 M NaOH and 0.01 M HCI. Two different background conditions, DI water and 0.01 M NaCI, were used. Results shown in Figure 7 indicate that maximum P removal occurs around pH 6.5 for both the background electrolyte systems. With zero background, percent removal increased slightly with an increase in pH and reached a maximum at pH » 6.5, and then decreased at higher pH values. This trend in P sorption is due to the pH-dependent speciation of ortho-phosphate, decrease in surface charge of PAA-bark with increasing pH (Fig. 2) and competitive effects exhibited by the hydroxyl ion. At pH values between 4.3 and 6.5, H_2PO_4 would be the dominant species. The fraction of $H_2PO_4^-$ decreases within this pH range, while the trend is opposite for HPO_4^{2-}. Being a divalent ion, HPO_4^{2-} would be subjected to a stronger electrostatic attractive force than $H_2PO_4^-$.

A comparison of the P sorption characteristics of PAA-bark against other well-known sorbents was performed using results obtained in our laboratory and by other researchers. Celi et al. (2001) reported a sorption maximum of 2.83 mg P/g for goethite in the presence of 0:01 M KCI and we obtained a value of 2.66 mg P/g for poor-crystalline gibbsite in a DI water background. PAA-bark compares favorably to both these sorbents with a maximum capacity of 1 1.96 and 7.62 mg P/g fiber in the presence of DI water and 0.01 M NaCI, respectively. In addition, PAA-bark interacts more effectively with P in the circum-neutral pH range, which is a significant advantage over other anionic sorbents, such as, AI oxide (Nemeth et al., 1998) and goethite (Celi et al., 2001). Maximum P sorption to AI oxide and goethite occurs at pH 4.2 and 4.5, respectively.

V. CONCLUSIONS

Chemical modification using PAA□HCl appears effective to develop anion exchange characteristics in bark fibers. This treatment resulted in a structural rearrangement, increase in surface energy and cationization of the fibers. Percent P removal decreased with an increase in initial P concentration for all the background conditions tested. Batch sorption data could be explained using Langmuir, Freundlich, and multi-site Langmuir models. Two distinct sorption regions were observed corresponding to the involvement of high affinity sites at low equilibrium P concentrations (C_e), and low affinity sites at high C_e levels. Maximum overall P sorption capacity of PAA-bark in the presence of DI water (zero background), 0.001 M NaCI, 0.01 M NaCI, and PAA-wood (DI water background) was 11.96, 8.11, 7.62, and 7.45 mg P/g fiber, respectively. PAA-bark exhibited a higher affinity for P than PAA-wood. Even in the presence of high levels of competing anion (i.e., Cl^-) at 0.01 M /, PAA-bark still sorbed more P than PAA-wood. Influence of pH was pronounced only in the case where DI water was used as the background. Highest sorption efficiency was observed at pH 6.5 for PAA-bark in the absence of any background electrolytes. Results obtained using complementary microscopic and macroscopic experimental techniques indicate that the modification of lignocellulosic materials by PAA imparts anion exchange characteristics and these modified fibers could function as effective P sorbents.

VI. ACKNOWLEGMENTS

Financial support provided for this project by the USDA Forest Service Forest Products Laboratory, Madison WI, the Massachusetts Department ,of Food and Agriculture, the Cranberry Institute and the Wisconsin Cranberry Board is gratefully acknowledged.

VII. REFERENCES

Adhesives & Sealants industry. 2001, New technology underway to develop bark-based adhesives. *[http:/www.adhesivesmag.com/asi/cda/articleinformation/features/bnp_features_item/0,2101,21764,00.html]*

APHA [American Public Health Association]. 1992. *Standard methods for the examination of water and wastewater.* 18th ed. APHA/AWWA/WPCF, Washington, DC.

Bailey, S.E., Olin, T.J., Bricka, R.M., and D.D. Adrian. 1999. A Review of Potentially Low-cost Sorbents for Heavy Metals. *Wat. Res.* 33:2469-2479.

Bohn H. L., B. L. Mcneal, and G. A. O'connor. 1985. *Soil Chemistry,* 2nd Edition, John Wiley & Sons, New York, NY.

Bras, I.P., Santos, L., and A. Alves. 1999. Organochlorine pesticides removal by pinus bark sorption. *Environ. Sci. Technol.* 33:631-634.

Carpenter, S.R., Caraco, N.F., Correll, D.L., Howarth, R.W., Sharpley, A.N., and V.H. Smith. 1998. Nonpoint pollution of surface waters with phosphorus and nitrogen. *Ecological Applications.* 8:559-568.

Celi L., M. Presta, F. Ajmore-Marsan, and E. Barberis. 2001. Effects of pH and Electrolytes on Inositol Hexaphosphate Interaction with Goethite. *Soil Sci. Soc. Am. J.* 65:753-760.

Daniel, T.C., Sharpley, A.N., Edwards, D.R., Wedepohl, R., and J.L. Lemunyon. 1994. Minimizing surface water eutrophication from agriculture by phosphorus management. *J. of Soil and Water Conserv. Supplement.* 49:30-38.

Daniel, T.C., Sharpley, A.N., and J.L. Lemunyon. 1998. Agricultural phosphorus and eutrophication: A symposium overview. *J. Environ. Qual.* 27:251-257.

Dillaha, T.A., Reneau, R.B., Mostaghimi, S., and D. Lee. 1989. Vegetative filter strips for agricultural nonpoint source pollution control. *Trans. ASAE.* 32:513-519.

Edgehill, R.U. and G.Q. (Max) Lu. 1998. Adsorption characteristics of carbonized bark for phenol and pentachlorophenol. *J. Chem. Technol. Biotechnol.* 71:27-34.

Forestry Chronicle, 1998. New life for tree bark. 74:34.

Ge, J. 2000. Biodegradable polyurethane materials from bark and starch. 1. Highly resilient foams. *J. Appl Polym. Sci.* 77:2575-2580.

Gloaguen, V. and H. Morvan. 1997. Removal of heavy metal ions from aqueous solution by modified barks. *J. Environ. Sci. Health.* A32:901-912.

Hayes K. F., C. Papelis and J. O. Leckie. 1987. Modeling Ionic Strength on Anion Adsorption at Hydrous Oxide/Solution Interfaces. *J. Colloid Interface Sci.* 125:717-726.

Hogue, C. 2000. Clearing the water. *Chemical and Engineering News.* March, p 31-33.

Kioussis, D.R., Wheaton, F.W., and P. Kofinas. 1999. Phosphate binding polymeric hydrogels for aquaculture wastewater remediation. *Aquacultural Engineering.* 19:163-178.

Krishnan, R., Rios, R., Salinas, N., and C. Duran-de-Bazua. 1998. Treatment of maize processing industry wastewater by percolating columns. *Environ. Tech.* 19:417-424.

Laszlo, J.A. and F.R. Dintzis. 1994. Crop residues as ion-exchange materials. Treatment of soybean hull and sugar beet fiber (Pulp) with epichlorohydrin to improve cation-exchange capacity and physical stability. *J. Applied Poly. Sci.* 52:531-538.

Leppert, D. 1990. Heavy metal sorption with clinoptilolite zeolite: alternatives for treating contaminated soil and water. *Mining Eng.* 42:604-608.

Leusch, A., Holan, Z.R., and B. Volesky. 1995. Biosorption of heavy metals (Cd, Cu, Ni, Pb, Zn) by chemically-reinforced biomass of marine algae. *J. Chem. Tech. Biotechnol.* 62:279-288.

Martin, R.E. 1969. Characterization of Southern Pine Barks. *Forest Products J.* 19:23-30.

Martin-Gullon, I. and R. Font. 2001, Dynamic pesticide removal with activated carbon fibers. *Wat. Res.* 35:516-520.

Masri, M.S., Reuter, F.W., and M. Friedman. 1974. Binding of metal cations by natural substances. *J. Appl. Polymer Sci.* 18:675-681.

McGinnis, G.D. and S. Parikh. 1975. The Chemical Constituents of Loblolly Pine Bark. *Wood Sci.* 7:295-297.

McKay G., Porter, J.F. and G.R. Prasad. 1999. The removal of dye coours from aqueous solutions by adsorption on low-cost materials. *Water, Air, Soil Pollution.* 114:423-438.

Moore, P.A., Jr. and D.M. Miller. 1994. Decreasing Phosphorus Solubility in Poultry Litter with Aluminum, Calcium, and Iron Amendments. *J. Environ. Qual.* 23:325-330.

Morais, L.C., Freitas, O.M., Goncalves, E.P., Vasconcelos, L.T., and C.G. Gonzales Beca. 1999. Reactive dyes removal from wastewaters by adsorption on eucalyptus bark: variables that define the process. *Wat. Res.* 33:979-988.

Nemeth Z., L. Gances, and G. Gernes. 1998. pH Dependence of Phosphate Sorption on Aluminum. *Corrosion Science.* 40:2023-2027.

Nickles, W.C. and J.W. Rowe. 1962. Chemistry of Western White Pine Bark. *Forest Products Journal.* 12:374-376.

Novotny, V. and H. Olem. 1994. *Water Quality - Prevention, Identification, and Management of Diffuse Pollution.* Van Nostrand Reinhold, New York. pp 41-43.

NRC (National Research Council). 1992. *Restoration of Aquatic Ecosystems: Science, Technology and Public Policy.* National Academic Press, Washington, DC.

Passialis, C.N., and Voulgaridis, E.V. 1999. Water repellent efficiency of organic solvent extractives from Aleppo pine leaves and bark applied to wood. *Holzforschung,* 53:151-155.

Pote, D.H., Daniel, T.C., Sharpley, A.N., Moore, P.A.Jr., Edwards, D.R., and D.J. Nichols. 1996. Relating extractable soil phosphorus to phosphorus losses in runoff. *Soil Sci. Soc. Am. J.* 60:855-859.

Schindler, D.W. 1977. Evolution of phosphorus limitation in lakes. *Science.* 195:260-262.

Sharpley, A.N., Chapra, S.C., Wedepohl, R., Sims, J.T., and T.C. Daniel. 1994. Managing agricultural phosphorus for protection of surface waters: issues and options. *J. Environ. Qual.* 23:437-451.

Sharpley, A.N., Daniel, T.C., Sirns, J.T., and D.H. Pote. 1996. Determining environmentally sound soil phosphorus levels. *J. Soil and Water Conserv.* 51:160-166.

Sharpley, A.N., Gburek, W., and L. Heathwaite. 1998. Agricultural phosphorus and water quality: sources, transport and management. *Agricultural and Food Science in Finland.* 7:297-314.

Sharpley, A.N., Daniel, T., Sims, T., Lemunyon, J., Stevens, R., and R. Parry. 1999. *Agricultural Phosphorus and Eutrophication.* United States Department of Agriculture, Agricultural Research Service, ARS-149.

Snoeyink, V.L. and D. Jenkins. 1980. *Water Chemistry.* John Wiley & Sons, New York, NY.

Snoeyink, V.L. 1990. Adsorption of organic compounds. In F.W. Pontius (ed.) *Water Quality and Treatment.* McGraw-Hill, Inc. New York. pp. 781-876.

Srivastava, S.K., Singh, A.K., and A. Sharma. 1994. Studies on the uptake of lead and zinc by lignin obtained from black liquor - a paper industry waste material. *Environ. Technol.* 15:353-361.

Syers J. K., M.G. Browman, G. W. Smillie, and R. B. Corey. 1973. Phosphate Sorption by Soils Evaluated by the Langmuir Adsorption Equation. *Soil Sci. Soc. Amer. Proc.* 37:358-363.

Teles de Vasconcelos, L.A. and C.G. Gonzalez Beca. 1993. Adsorption equilibria between pine bark and several ions in aqueous solution, 1. Pb(ll). *Eur. Water Poll. Control.* 4:41-51.

USDA Forest Service, 1997. Forest lnventory and Analysis. Timber Product Output Database Retrieval System.

U.S. EPA (United States Environmental Protection Agency). 1990. *National Water Quality Inventory, Report to Congress.* Office of Water, U.S. Government Printing Office, Washington DC.

U.S. EPA (United States Environmental Protection Agency). 1996. *Environmental lndicators of Water Quality in the United States.* EPA 841-R-96-002, USEPA, Office of Water, U.S. Government Printing Office, Washington DC.