

Removal of phosphorus using AMD-treated lignocellulosic material

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Abstract

Excess nutrients, including phosphorus, can cause eutrophication in surface water and reservoirs. We tested the phosphate removal capacity of juniper fiber through isotherm, kinetic, column, and field tests. Heavy metals from an acid mine drainage (AMD) site were precipitated on the surface of juniper fiber. The modified fiber was tested in laboratory-scaled batch and column tests. Elemental analysis showed that soluble iron species deposited on the modified fiber acted as an inorganic adsorbent for anions; sorption capacity of this juniper fiber was higher than that of other conventional adsorbents. A pseudo second-order kinetic model fitted well for sorption of phosphorus onto the modified medium. The modified lignocellulosic material was used to remove phosphorus from wastewater from two dairy farms in the Catskill/Delaware watershed. The fiber was installed inside a filter box, forming a nonwoven mat. Phosphorus removal efficiency of the material was about 41 percent at 59 mg/L of influent phosphorus concentration.

The quality of water reservoirs in the Catskill/Delaware watershed is affected by run-off from approximately 350 dairy and livestock farms and 90 other agricultural enterprises. Small dairy farms discharge a considerable amount of phosphorus to the watershed; the total maximum daily load of phosphate is not limited for individual farms. Wastewater from the milking system is drained directly to the land. In addition to phosphorus, wastewater includes sediment and may include parasites of the genus *Cryptosporidium*.

Excess nutrients, including phosphorus, can cause eutrophication in surface water and reservoirs (NYCDEP 1991a, 1991b, 2001; Hammer and Hammer 2001). In natural, domestic, and industrial treatment systems, phosphorus can be removed by adsorption, chemical precipitation, and biological treatment (Morse et al. 1990). Among industrial treatment technologies, adsorption on a fixed-bed filtration system is commonly used to purify wastewater with a low concentration of phosphorus (Hano et al. 1997). Diverse adsorbents, such as red mud, activated alumina, polymeric ligand exchangers, iron/aluminum-coated sand, and calcium-based adsorbents, have been studied for their capacity to remove phosphate (Hano et al. 1997, Lo et al. 1997, Akay et al. 1998, Zhao and Sengupta 1998, Ayoub et al. 2001, Khadhraoui et al. 2002).

Lignocellulosic materials have the capacity to adsorb pollutants (Basso et al. 2002, Reddad et al. 2002). Chemical modification of these materials (i.e., saponification and phos-

phorylation) enhances their sorption capacity for heavy cationic metals in water (Drake et al. 1996, Tiemann et al. 1999, Romero-Gonzalez et al. 2001, Nada et al. 2002). For removal of anions such as phosphate, lignocellulosic materials have been cationized through hybridizing with inorganic chemicals as well as grafting with ammonium-type chemicals. Zghida et al. (2002) used epoxy propyltrimethylammonium chloride (EPTMAC) grafted lignocellulosic materials to remove chromium oxy-anions. DeMarco et al. (2003) developed a polymeric/inorganic hybrid sorbent for removing arsenic. The hybrid sorbent was a polymeric cation exchanger containing agglomerates of nanoscale hydrated iron oxide. Likewise, iron (III)-loaded carboxylated polyacrylamide-grafted sawdust was tested for removing phosphate from an aqueous solution

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(Unnithan et al. 2002). The modification consisted of two steps: 1) graft copolymerization of acrylamide and N,N'-methylenebisacrylamide onto sawdust; and 2) attachment of iron (III) to the carboxylic acid moiety of the adsorbent. These methods require at least one chemical treatment to activate the capacity of lignocellulosic material to remove anions from water.

In previous work (Shin et al. 2004b), juniper chips were processed into a mat-type filter medium to restore the watershed affected by acid mine drainage (AMD) in the Wayne National Forest in Ohio. In general, AMD contains iron, sulfates, aluminum, manganese, and other dissolved and suspended solids because of its low pH (Draver 1997). Iron species were found to be the primary metal deposited onto the juniper filter mat, implying that juniper can be a natural and novel inorganic lignocellulosic hybrid adsorbent.

Juniper (*Juniperus monosperma*) fiber was chosen because of its relatively high sorption capacity for heavy metals (Han 1999). In addition, juniper is a small-diameter and underutilized wood as well as an invasive species, which contributes to fire loading. Another benefit is the fibrous character of juniper bark, which allows the bark to be processed with the wood; the wood does not need to be debarked before processing.

In the study reported here, we tested the phosphate removal capacity of juniper fiber through isotherm, kinetic, column, and field tests. The field tests consisted of installing small filtration systems on two dairy farms in the Catskill/Delaware watershed.

Materials and methods

Materials

Juniper trunks and branches, including bark, were shredded into small chips, refined (fiberized or mechanically pulped), and made into a Rando mat using 10 percent of HC-105 binder (Hoechst Celanese Inc. Germany), which is the most widely used polymer binder in the geotextile industry. The fiber was washed with 0.5-M sodium hydroxide twice, after chipping and after formation of the Rando mat. Mat density was 0.109 to 0.131 g/cm³ and thickness was about 1.3 cm. The mat was cut into 61-cm by 61-cm pieces (mats). Mats were initially exposed to AMD for 3 days at the Wayne National Forest. They were then dried and shipped to the Forest Products Laboratory in Madison, Wisconsin. Mats were washed with distilled water to remove excess water-soluble components and dried. All mats except those used for the laboratory-scale tests were shipped to the field site in New York State to be reused for removing phosphorus from water.

Unmodified and chemically modified filter mats were subjected to isotherm, kinetic, and column tests in the laboratory. The unmodified mats are simply designated as "juniper." The modified mats are designated as base-treated juniper. Base-treated mats were treated with 0.5 M sodium hydroxide for 24 hours to improve cation exchange capacity (CEC). This increased CEC could enhance the binding ability of iron species, which can bind with phosphate in water. The mechanism of the base treatment is described in detail in Min et al. (2004). The WNF-designated mats were treated with sodium hydroxide and exposed to AMD in the Wayne National Forest: WNF01 mats were untreated and WNF02 mats were treated with water to remove soluble components and then redried. All mats were ground with a Wiley mill to pass a 20-mesh

screen and sieved again with a 20-mesh screen for adsorption tests.

Elemental analysis and adsorption tests

Inductively coupled plasma atomic emission spectrometry (ICP-AES, ULTIMA, Jobin Yvon Inc., Edison, NJ) was used for elemental analysis of inorganic components in solid and solution samples. Phosphorus isotherms were acquired through batch experiments. The 20-mesh powdered samples, weighing 0.1 to 1.0 g, were placed in 125-mL bottles; 50 mL of 10mg/L-phosphorus solutions was added. Ionic strength of the solution was maintained at 0.01 M using sodium nitrate. The samples were sealed and placed in a shaker (Bigger Bill Oscillator, Thermolyne, 1A) and shaken at 150 rpm for 1 day at 25°C. After 48 hours of shaking, the suspension was filtered immediately through a 0.45- μ m microfilter, and phosphorus concentration in filtrate was analyzed by ICP-AES.

Adsorption kinetic experiments were performed using 1000-mL solutions with 2.0 g of 20-mesh sample. Initial phosphorus concentration of the solution was 10 mg/L; pH of the solution was maintained at 6.4 using nitric acid or sodium hydroxide solution. The suspension was stirred with a magnetic bar, and samples were taken at various times over a period of 5 hours. Change in phosphorus concentration was measured by ICP-AES.

Column test

A column test was conducted using an intact Rando mat rather than powdered sample. Juniper mats charged with iron species at the Wayne National Forest were removed from the filtration boxes, washed with water, dried, and cut into 4.5-cm-diameter plugs. The pH of the phosphorus solution was adjusted to 7 with 0.1 M nitric acid and sodium hydroxide solution. Five plugs were weighed, packed into a 4.5-cm-diameter, 20-cm-long glass column, and eluted with 30 mg/L phosphorus solution (potassium dihydrogenphosphate, +98%, Aldrich, Milwaukee, WI) with a Minipuls 3 fraction collector (Gilson, Milwaukee, WI) pump at a flow rate of 4 mL/min. A 204 Gilson fraction collector was used to collect 20-mL aliquots. The weight of the plugs, phosphorus concentration, total volume of standard solution to be eluted, and flow rate were determined on the basis of practical experience; total elution time was arbitrarily limited to 15 hours so that an experiment could be finished overnight. The process was replicated six times.

Field test

The filtration system was installed at two farms in the Catskill/Delaware watershed. The system with the WNF02 mats was connected to the wastewater drainage pipe from the milking system. The first field test was 3 days long at a farm that discharges phosphorus in a range of 60 mg/L. The second field test was 12 days long at a farm that discharges phosphorus in a range of 100 mg/L.

The filtration box was designed at the Forest Products Laboratory and made of fiberglass by a commercial builder (Empire Fiberglass Products Inc., Little Falls, NY). The filter frames were fitted into slots in the box, and 10 filter mats were placed inside the box (**Fig. 1**). Flow through the filter mats was mathematically modeled by Hur et al. (2003). Water samples were collected twice a day at the inlet of the filtration box. The samples were analyzed for total dissolved phosphorus by ICP-AES.

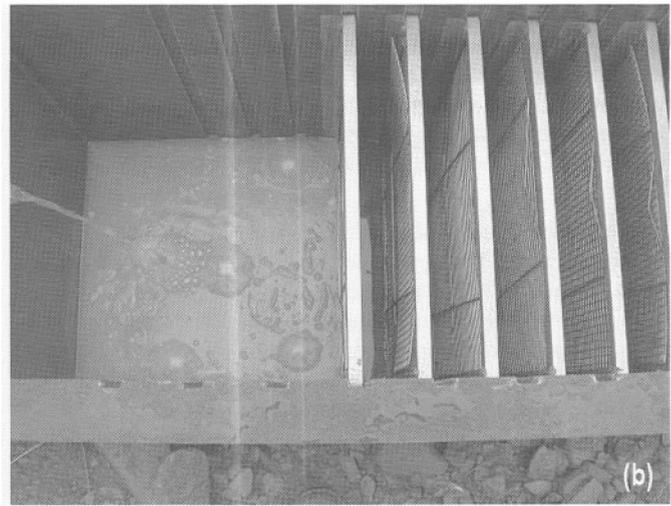


Figure 1. – Lignocellulosic filtration system: a) filtration box, b) filter frames inside filtration box.

Table 1. – Elemental analysis of inorganic components of filter mats.

Sample	Contents				
	Al	Fe	Pb	S	Zn
	------(mg/g)-----				
Juniper	0.112	4.670	0.177	4.592	0.100
Base-treated juniper	0.116	6.533	0.184	4.763	0.103
WNF01	0.103	129.5	0.169	8.466	0.102
WNF02	0.076	134.9	0.254	7.027	0.068

Results and discussion

Elemental analysis

Table 1 shows inorganic component content of the filter mats. Iron content of juniper and base-treated juniper mats was 4.670 and 6.533 mg/g, respectively. Iron content of mats exposed to AMD was 129.5 and 134.9 mg/g for WNF01 and WNF02 mats, respectively, or about 13 percent by weight of iron species. The content of other inorganic components was similar before and after exposure to AMD.

Several mechanisms might be responsible for the deposition of iron species on filter mats (Tiemann et al. 1999, Reddad et al. 2002). Iron species are deposited on the filter surface through chemical interactions such as replacement of calcium ions and adsorption on active sites (e.g., phenolic or carboxylate sites). The mats also physically block solid particles by putting them into suspension.

Adsorption behavior

Figure 2 shows the kinetic behavior of each sample. As expected, the phosphorus sorption capacity of the unmodified juniper and base-treated juniper samples was almost nil. In contrast, the kinetic data for WNF01 and WNF02 show that modification with iron greatly increased sorption capacity for phosphorus. Most uptake of phosphorus occurred within 100 min, after which sorption of phosphorus reached an equilibrium state.

The results of fitting the adsorption data to several kinetic equations (Tiemann et al. 1999, Romero-Gonzalez et al. 2001, Reddad et al. 2002) are shown in Table 2. Based on the determination coefficients for each model, the pseudo second-

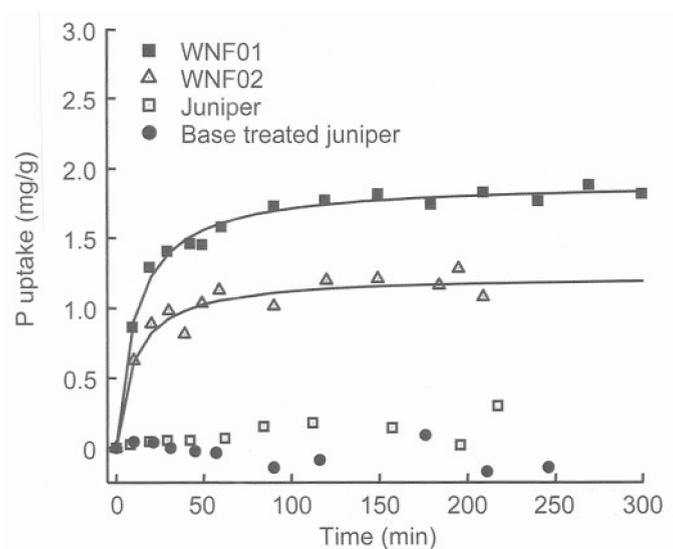


Figure 2. – Kinetics of phosphorus adsorption for each sample (Shin et al. 2004a).

Table 2. – Determination coefficients for each model equation.

Sample	Pseudo 1st r^2	Pseudo 2nd		Power function r^2	Simple Elovich r^2	Parabolic diffusion r^2
		r^2	K (g/mg/min)			
WNF01	0.906	0.998	0.0526	0.923	0.911	0.930
WNF02	0.914	0.983	0.0809	0.769	0.769	0.942

order model and the parabolic diffusion model matched well with the kinetic data. Since the parabolic diffusion equation was induced from diffusion-controlled adsorption, its good fit to the data suggests that the kinetics of phosphorus sorption on WNF01 and WNF02 was controlled by diffusion. The pseudo second-order model also fitted the kinetic data well, showing a kinetic constant K of 0.0526 and 0.0809 mg/g/min for WNF01 and WNF02, respectively, which indicates that adsorption on the filter medium is closer to chemisorption than physisorption (Ho and McKay 2000).

Adsorption data were fitted to both Langmuir and Freundlich isotherms, as expressed in Equations [1] and [2], respectively:

$$q_{eq} = \frac{bQ_{max}C_{eq}}{1 + bC_{eq}} \quad [1]$$

where q_{eq} = amount adsorbed at equilibrium (mg/g); Q_{max} = maximum adsorbate loading (mg/g); C_{eq} = equilibrium concentration; b = constant.

$$q_{eq} = KC_{eq}^n \quad [2]$$

where K and n are constants.

Isotherms for phosphorus adsorption and fitted results are shown in **Figure 3** and **Table 3**. The determination coefficient

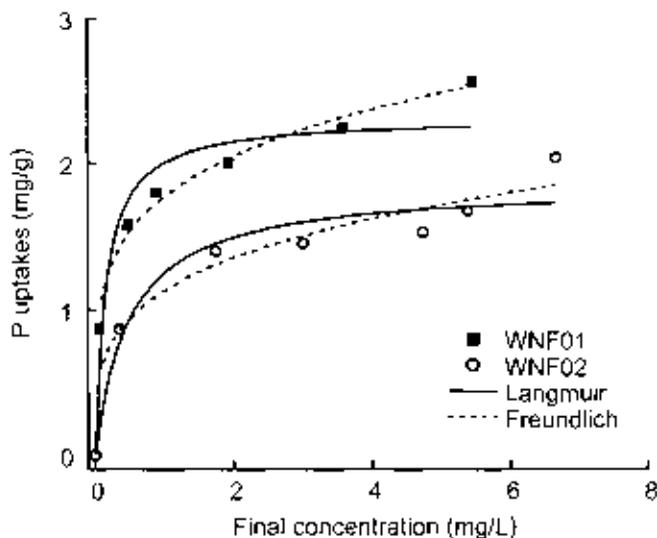


Figure 3. — Isotherms of phosphorus adsorption for each sample and fitted lines (Shin et al. 2004a).

Table 3. — Parameters from fit of isotherms to Freundlich and Langmuir models.

Sample	Freundlich		Langmuir			
	K	$1/n$	Q_{max} (mg/g)	b	r^2	
WNF01	1.76	0.211	0.986	2.31	6.41	0.947
WNF02	1.12	0.260	0.891	1.85	2.06	0.942

Table 4. — Phosphorus sorption capacity of diverse filter media.

Sorbent	Type	Q_{max} (mg/g)	Reference
Kandiustalf	Kaolinite, Fe oxides	0.394	Brady et al. 1990
Matapeake	Chlorite, kaolinite, Fe oxides	0.465	Brady et al. 1990
Trophumults	Fe, Al oxides, kaolinite	2.060	Brady et al. 1990
Iron and aluminum oxide coated sand	Fe, Al oxides	0.011 to 0.033	Ayoub et al. 2001
Iron and aluminum oxide coated olivine	Fe, Al oxides	0.015 to 0.035	Ayoub et al. 2001
Geothite	Fe oxides	1.3 ^a	Baker et al. 1998
AA300G	γ Al oxides	2.0 ^a	Baker et al. 1998
C-70	α Al oxides	1.0 ^a	Baker et al. 1998

^aCalculated on basis of results reported in the literature.

do not indicate which isotherm model is dominant in the isotherm data. The Q_{max} (maximum adsorbate loading onto adsorbent) values of WNF01 and WNF02 (2.31 and 1.85 mg/g, respectively) indicate that mild washing with water reduced the phosphorus sorption capacity of the filter medium. A similar phenomenon was observed in the kinetic results. The sorption capacity of the modified lignocellulosic filters, in particular of WNF01, is superior to that of other inorganic filter media, **Table 4** lists the phosphorus sorption capacity of various filters reported in the literature (Baker et al. 1998, Brady and Weil 1999, Ayoub et al. 2001).

Column test

A column test was conducted to evaluate the adsorption capacity of the filter medium from flowing water. As long as iron species were present in the medium, the medium was able to adsorb phosphorus. In **Figure 4**, P is the concentration of the 30-mg/L phosphorus solution after passing through the filter medium. P_{net} is the amount of phosphorus adsorbed by the medium, which is the difference between 30 mg/L and P . As iron was depleted from the filter, adsorption of phosphorus decreased. Phosphorus concentration started to increase after 20 mL of solution had passed through the filter. The maximum phosphorus adsorption capacity was calculated as 3 to 4 mg/g. Iron was adsorbed by the addition of the cation-exchanging base-treated juniper medium, as shown in **Figure 5**.

Field test

In the laboratory tests, only inorganic phosphorus was used as an adsorbate. However, phosphorus in wastewater exists in several forms: particular, organic, inorganic, total, and so on. In the field test, phosphorus concentration refers to the amount of total dissolved phosphorus; each water sample was filtered by a 0.45- μ m filter prior to analysis. The mechanism of phosphorus removal in the field is more complicated than the physiochemical mechanism in the laboratory. In addition to adsorption, another possible mechanism for phosphorus removal in the field is biological, by the action of microorganisms on the surface of lignocellulosic filter mats. According to Chiou et al. (2001) and Morgenroth and Wilderer (1998), phosphorus is removed by a biofilm that forms on a support material, in this case the lignocellulosic filter medium.

Table 5 shows the performance of filter mats installed on a farm for 3 days in 2002. Removal efficiency varied in daily sampling; the average removal efficiency of WNF02 was 41.51 percent at 59.19 mg/L of inlet phosphorus concentration. This experiment was repeated in 2003 for an extended period (12 days) on a farm where the inlet phosphorus concentration was about 100 mg/L (**Table 6**). Average removal efficiency on this farm was only 25 percent, which indicates that the capacity of the filter medium was dependent on phosphorus concentration.

The field test results suggest that a filtration system containing lignocellulosic-based filters could lower the amount of phosphorus load from a farm to the watershed by about 25 to 40 percent within the range of phosphorus concentration experi-

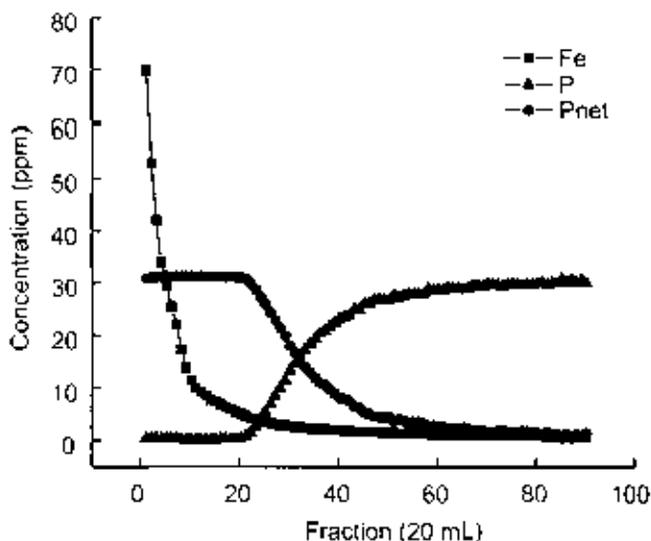


Figure 4. – Elution of 30 mg/L phosphorus standard solution as a function of fraction.

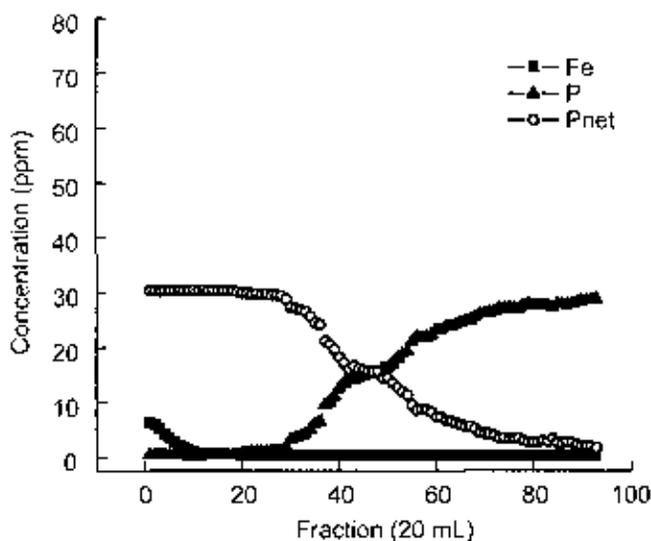


Figure 5. – Elution of 30 mg/L phosphorus standard solution as a function of fraction. Cation exchanger added at end of column to control iron.

enced in this study. During the test period, we did not observe any deterioration of the phosphorus-removal capacity of the fiber mats.

Conclusion

The capacity of juniper fiber for removing phosphorus from wastewater was evaluated in this study. Phosphorus sorption capacity was increased by modifying the lignocellulosic filter mats with iron species. Further research on chemical modification would be necessary for enhancing phosphorus removal. In the isotherm test, maximum adsorbate loading (Q_{max}) onto adsorbent was as high as 2.31 mg/g, which is comparable to or better than that of other natural filter media. Maximum sorption capacity was about 3.5 mg/g in the column test, but some iron was released during the reaction. In field tests, lignocellulosic filter mats removed about 40 percent of phosphorus from a waste stream containing around 60 mg/L phosphorus and 25 percent phosphorus from a waste

Table 5. – Phosphorus analysis of water sample taken at inlet and outlet of filter box in 2002.

Sampling in 2002	Concentration of total dissolved phosphorus			Removal efficiency (%)
	Inlet	Outlet	Difference	
	----- (mg/L) -----			
Day 1 a.m.	57.55	34.89	22.65	39.36
p.m.	57.57	19.87	37.70	65.48
Day 2 a.m.	56.41	31.41	24.99	44.30
p.m.	59.76	44.02	15.73	33.60
Day 3 a.m.	64.68	42.94	21.73	33.60
Avg. value	59.19	34.62	24.57	41.51

Table 6. – Phosphorus analysis of water sample taken at inlet and outlet of filter box in 2003.

Sampling in 2003	Concentration of total dissolved phosphorus			Removal efficiency (%)
	Inlet	Outlet	Difference	
	----- (mg/g) -----			
Day 1 a.m.	92.64	60.62	32.02	34.56
p.m.	73.44	55.96	17.47	23.80
Day 2 a.m.	96.61	72.64	23.97	24.81
p.m.	78.73	62.50	16.23	20.61
Day 3 a.m.	86.61	64.98	21.64	24.98
p.m.	96.22	76.32	19.90	20.68
Day 4 a.m.	99.01	69.11	29.90	30.20
p.m.	95.77	83.29	12.48	13.03
Day 5 a.m.	93.17	74.78	18.39	19.73
p.m.	76.95	66.68	10.27	13.35
Day 6 a.m.	76.96	62.70	14.26	18.53
p.m.	78.96	63.37	15.59	19.74
Day 7 a.m.	119.06	106.07	12.99	10.91
p.m.	125.07	97.91	27.16	21.71
Day 8 a.m.	72.64	44.39	28.25	38.88
p.m.	82.12	57.77	24.34	29.65
Day 9 a.m.	89.16	59.58	29.58	33.17
p.m.	89.79	58.73	31.06	34.60
Day 10 a.m.	125.64	89.95	35.69	28.41
p.m.	89.34	59.41	29.93	33.50
Day 11 a.m.	93.93	75.12	18.81	20.03
p.m.	94.09	76.40	17.70	18.81
Day 12 a.m.	210.95	141.10	69.85	33.11
p.m.	140.43	84.70	55.73	39.68
Avg. value	99.05	73.50	25.55	25.27

stream containing 100 mg/L. This system is relatively inexpensive and there is room for improvement.

Literature cited

- Akay, G., B. Keskinler, A. Cakich, and U. Danis. 1998. Phosphate removal from water by red mud using crossflow microfiltration. *Water Res.* 32(3):717-726.
- Ayoub, G.M., B. Koopman, and N. Pandya. 2001. Iron and aluminum hydroxy (oxide) coated filter media for low-concentration phosphorus removal. *Water Environ. Res.* 73:478-485.
- Baker, M.J., D.W. Blowes, and C.J. Ptacek. 1998. Laboratory development of permeable reactive mixtures for the removal of phosphorus from onsite wastewater disposal systems. *Environmental Sci. & Tech.* 32:2308-2316.

- Basso, M.C., E.G. Cerrella, and A.L. Cukierman. 2002. Lignocellulosic materials as potential biosorbents of trace toxic metals from wastewater. *Ind. Eng. Chem. Res.* 41:3580-3585.
- Brady, N.C. and R.R. Weil. 1999. *The Nature and Properties of Soils*. 12th ed. Prentice-Hall, Inc., Upper Saddle River, NJ.
- Chiou, R.J., C.F. Ouyang, K.H. Lin, and S.H. Chuang. 2001. The characteristics of phosphorus removal in an anaerobic/aerobic sequential batch biofilter reactor. *Water Sci. & Tech.* 44(1):57-65.
- DeMarco, M.J., A.K. Sengupta, and J.E. Greenleaf. 2003. Arsenic removal using a polymeric/inorganic hybrid sorbent. *Water Res.* 37: 164-176.
- Drake, L.R., S. Lin, and P.J. Rayson. 1996. Chemical modification and metal binding studies of *Datura innoxia*. *Environmental Sci. & Tech.* 30:110-114.
- Draver, J.I. 1997. *The Geochemistry of Natural Waters: Surface and Groundwater Environments*. 3rd ed. Prentice Hall, Inc., Upper Saddle River, NJ.
- Hammer, M.J., Sr. and M.J. Hammer, Jr. 2001. *Water and Wastewater Tech.* 4th ed. Prentice Hall, Inc., Upper Saddle River, NJ.
- Han, J.S. 1999. Stormwater filtration of toxic heavy metal ions using lignocellulosic materials: Selection process, fiberization, chemical modification and mat formation. *In: Proc., 2nd Inter-Regional Conf. on Environment - Water 99*, Lausanne, Switzerland.
- Hano, T., H. Takanash, M. Hirata, K. Urano, and S. Eto. 1997. Removal of phosphorus from wastewater by activated alumina adsorbent. *Water Sci. & Tech.* 35:39-46.
- Ho, Y.S. and G. McKay. 2000. The kinetics of sorption of divalent metal ions onto sphagnum moss peat. *Water Res.* 34(3):735-742.
- Hur, N., B. Choi, J.S. Han, E.W. Shin, S. Min, and R.M. Rowell. 2003. A numerical simulation on the flow of watershed filtration reactors using lignocellulosic materials. *In: Proc., 6th Inter-Regional Conf. on Environment - Water, Envirowater, Albacete, Spain.*
- Khadhraoui, M., T. Watanabe, and M. Kuroda. 2002. The effect of the physical structure of a porous Ca-based sorbent on its phosphorus removal capacity. *Water Res.* 36:3711-3718.
- Lo, S.-L., H.-T. Jeng, and C.-H. Lai. 1997. Characteristics and adsorption properties of iron-coated sand. *Water Sci. & Tech.* 35:63-70.
- Min, S.H., J.S. Han, E.W. Shin, and J.K. Park. 2004. Improvement of cadmium ion removal by base treatment of juniper fiber 1. *Water Res.* 38:1289-1295.
- Morgenroth, E. and P.A. Wilderer. 1998. Modeling of enhanced biological phosphorus removal in a sequencing batch biofilm reactor. *Water Sci. & Tech.* 37(4-5):583-587.
- Morse, G.K., S.W. Brett, J.G. Guy, and J.N. Lester. 1990. Review: Phosphorus removal and recovery technologies. *Sci. Total Environ.* 212:69-81.
- Nada, A.M.A., M.A. Eid, R.M. El Bahnasawy, and M.N. Khalifa. 2002. Preparation and characterization of cation exchangers from agricultural residues. *J. Appl. Polym. Sci.* 85:792-800.
- New York City Dept. of Environmental Protection (NYCDEP). 1999a. Methodology for calculating phase II total maximum daily loads (TMDLs) of phosphorus for New York City drinking water reservoirs. NYCDEP, New York.
- _____. 1999b. Development of a water quality guidance value for phase II total maximum daily loads (TMDLs) in New York City reservoirs. NYCDEP, New York.
- _____. 2001. Nonpoint source implementation of the phase II TMDLs. NYCDEP, New York.
- Reddad, Z., C. Gerente, Y. Andres, M.C. Ralet, J.F. Thibault, and P. Le Cloirec. 2002. Ni(II) and Cu(II) binding properties of native and modified sugar beet pulp. *Carbohydrate Polymers* 49(1):23-31.
- Romero-Gonzalez, M.E., C.J. Williams, and P.H.E. Gardiner. 2001. Study of the mechanisms of cadmium biosorption by dealginated seaweed waste. *Environmental Sci. & Tech.* 35(14):3025-3030.
- Shin, E.W., J.S. Han, and S.H. Min. 2004a. Removal of phosphorus from water using lignocellulosic material modified with iron species from acid mine drainage. *Environmental Tech.* 25(2):185-191.
- _____, M. Jang, S.H. Min, J.K. Park, and R.M. Rowell. 2004b. Phosphate adsorption on Al-impregnated mesoporous silicates: Surface structure of adsorbents and adsorption behaviors. *Environmental Sci. & Tech.* 38(3):912-917.
- Tiemann, K.J., J.L. Gardea-Torresdey, G. Gamez, K. Dokken, and S. Sias. 1999. Use of x-ray absorption spectroscopy and esterification to investigate Cr(III) and Ni(II) ligands in alfalfa biomass. *Environmental Sci. & Tech.* 33(1):150-154.
- Unnithan, M.R., V.P. Vinod, and T.S. Anirudhan. 2002. Ability of iron(III)-loaded carboxylated polyacrylamide-grafted sawdust to remove phosphate ions from aqueous solution and fertilizer industry wastewater: Adsorption kinetics and isotherm studies. *J. Appl. Polym. Sci.* 84:2541-2553.
- Zghida, H., M.H.V. Baouab, and R. Gauthier. 2002. Sorption of chromium oxy-anions onto cationized lignocellulosic material. *J. Appl. Polym. Sci.* 87:1660-1665.
- Zhao, D.Y. and A.K. Sengupta. 1998. Ultimate removal of phosphate from wastewater using a new class of polymeric ion exchangers. *Water Res.* 32(5): 1613-1625.