ELSEVIER
Ecological Engineering 15 (2000) 121–132
ECOLOGICAL ENGINEERING
www.elsevier.com/locate/ecoleng

Phosphorus removal by wollastonite: A constructed wetland substrate

Andrea S. Brooks [a], Melissa N. Rozenwald [a], Larry D. Geohring [a], Leonard W. Lion [b], Tammo S. Steenhuis [a,*]

[a] *Department of Agricultural and Biological Engineering, 226 Riley-Robb Hall, Cornell University, Ithaca, NY 14853, USA*
[b] *Department of Civil and Environmental Engineering, Cornell University, Ithaca, NY 14853, USA*

Received 7 August 1998; received in revised form 17 September 1999; accepted 22 October 1999

Abstract

Wollastonite, a calcium metasilicate mineral mined in upstate New York, is an ideal substrate for constructed wetland ecosystems for removing soluble phosphorus from secondary wastewater. Design parameters, required for designing a full-scale constructed wetland, were measured in vertical upflow columns with hydraulic residence times varying from 15 to 180 h. Secondary wastewater was pumped vertically upward through eleven soil columns, 1.5 m in length and 15 cm in diameter and influent and effluent concentrations of soluble phosphorus were monitored for up to 411 days. Greater than 80% removal (up to 96%) was observed in nine out of 11 columns and effluent concentrations of soluble phosphorus ranged from 0.14 to 0.50 mg/l (averaging 0.28 mg/l) when the residence time was >40 h. Columns with a decreased residence time averaged 39% removal. A direct relationship between residence time and soluble phosphorus removal was established.

Keywords: Tertiary wastewater treatment; Wastewater; Constructed wetlands; Phosphorus removal; Sewage; Water quality; Secondary sewage effluent; Loading rate

---

1. Introduction

Excessive phosphorus loading from manmade sources is commonly linked to eutrophication of lakes and streams (Hillbricht-Ilkowska et al., 1995). Phosphorus is contributed by agricultural runoff and erosion from agricultural land, urban runoff and the most easily manipulated source and focus of this paper, wastewater effluent. Although most communities in the USA have primary and secondary treatment, in the near future many of them will be required to have tertiary treatment, to reduce wastewater effluent concentrations of phosphorus (P) to levels as low as 1.0 mg/l (EPA, 1987). Very few ecosystems exist, that can reduce P to those levels.

The use of both natural and created wetlands as tools in the treatment of polluted waters, is increasing in popularity as an ecological engineering alternative to conventional, chemical based meth-

---

[*] Corresponding author. Tel.: +1-607-2552489; fax: +1-607-2554080.
E-mail address: tss1@cornell.edu (T.S. Steenhuis)

PII: S0925-8574(99)00056-7

ods (Mitsch and Jørgensen, 1989; Kadlec and Knight, 1996). Wetland ecosystems have the advantages of being self-perpetuating, low-maintenance and cost-efficient treatment systems (Fennessy and Mitsch, 1989). Constructed wetland ecosystems, offer better opportunities for wastewater treatment than natural wetlands (Verhoeven and Meuleman, 1999). In treating sewage water for small to medium sized communities, they can be used for reducing BOD and suspended solids from secondary wastewater (Reed and Brown, 1992; Kern and Idler, 1999; Verhoeven and Meuleman, 1999). P removal has been variable at best (Watson et al., 1989; Mann, 1990; Jenssen et al., 1993; Greenway and Woolley, 1999) because substrates are often selected based on local availability and particle size for reduced clogging, without consideration for their capacity for P removal (Watson et al., 1989; Mann, 1990). One of the ecotechnological means of attaining sufficient low P concentration, is the use of specialized substrates with physical and chemical properties conducive to P removal, while maintaining sufficient permeability (House et al., 1994). Specialized substrates used for P removal in wetlands, are pumice, sand, LECA (a reactive porous media) and industrial wastes such as blast furnace slag and fly ash (Jenssen et al., 1993; Mann and Bavor, 1993; Nur Onar et al., 1996). Wollastonite, a calcium metasilicate mined in northern New York state, is abundant and the tailings left after the production of pure wollastonite are inexpensive. Preliminary studies have shown promise for efficient P removal with Wollastonite tailings (Corrigan, 1993; Geohring et al., 1995). The mineral composition of wollastonite is reported to be close to 50% CaO (Buckley, 1997). P Removal in mediums, with high calcium content is typically attributed to either adsorption (Iannou et al., 1994; Nur Onar et al., 1996) or chemical precipitation of calcium phosphates (Hundal, 1988; House et al., 1994; Agbenin, 1996). Chemical precipitation of P by wollastonite is likely, as a stable mineral Hydroxyapatite ($Ca_5(PO_4)_3(OH)_{(s)}$). The equilibrium concentration of this compound can be as low as 5.9×10^{-4} μg/l as phosphorus (Brooks, 1997). Adsorption is also possible through either ion or ligand exchange at soil surfaces.

The use of wollastonite in constructed wetland ecosystems for P removal, requires the quantifying of the mechanism(s) facilitating P removal. Because these types of ecosystems are so complex (Mitsch and Jørgensen, 1989) the quantification of their reactions is initially best done, under well controlled conditions in the laboratory before full-scale implementation. Our first objective was, therefore, to obtain design parameter (such as required retention for optimal P removal). Because horizontal flow wetlands, may have overland flow complicating the interpretation of the results, we used a vertical upflow system. Soluble phosphorus removal was monitored over a wide range of residence times. A second objective of this research was to come to a more comprehensive understanding and characterization of the mechanism involved in P sorption from wollastonite, through the use of controlled laboratory batch experiments. Previous research has indicated that a lengthy residence time (days to weeks) facilitates high P removal in wetland systems (Jenssen et al., 1993). In order to maximize P removal, hydraulic residence times on a scale of days were included in this study.

2. Material and methods

2.1. Batch experiments

Simple batch experiments were performed, primarily to characterize the phosphorus removal mechanism of wollastonite. Time series batch experiments were conducted by mechanically agitating 125 ml sample bottles with a 20:1 solution/soil ratio (40 ml phosphate solution to 2 g of pure wollastonite) for designated periods of time ranging from 0.1 to 72 h and measuring the residual concentration of phosphate in solution. This was done at initial concentrations of both 5 and 10 mg/l. The soluble phosphorus was measured by the ascorbic acid method (APHA et al., 1985).

A second set of time series experiments was done, to determine the effects of calcium phosphate seeding on P removal. This was done by mixing 10 mg/l phosphate solution with 2 g of wollastonite and agitating the mixture for 3 days.

The wollastonite was then filtered out of the sample, using a 0.45 μm filter and then dried in an oven at 40°C for 24 h. The filtrate was analyzed for residual P concentration. The dried wollastonite was then used as a calcium phosphate 'seed' in kinetic experiments. One gram of the dried wollastonite and 1 g of 'new' wollastonite were combined and then mixed with a 5 mg/l phosphorus solution and the phosphorus concentration was monitored over 3 days.

2.2. Column experiments

Phosphorus removal by wollastonite was studied in vertical upflow columns of 1.5 m length. Columns were constructed with 15 cm diameter poly-vinylchloride (PVC) tubes, cut to 1.5 m lengths, with sampling ports located 10 cm from the top of each column. The columns were capped at the base with a circular piece of PVC with a port in the center, that served as the influent connection. Fig. 1 shows the general layout of a filled vertical upflow column. All experiments were run in a constant "temperature room" (18–21°C) in the Department of Agricultural and Biological Engineering at Cornell University.

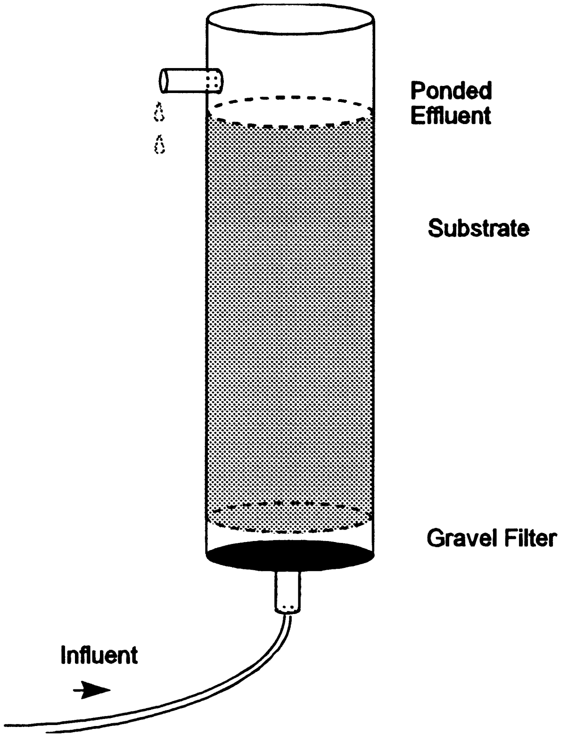

Fig. 1. Schematic of vertical upflow column.

The columns were filled in the following order: A wire screen was placed on the bottom of the column, followed by 15 cm of washed gravel, a second screen and then the column was filled with the wollastonite substrate up to ≈ 2 cm below the effluent sampling port.

The vertical upflow system consisted of peristaltic pumps and tubing, that ran from a wastewater source tank, through a sand filter and into the bottom port of a column. Secondary wastewater was pumped up through the wollastonite matrix to ≈ 2 cm below the effluent port, where the water was allowed to pond to obtain average effluent concentrations from the sampling port.

The inflow system consisted of irrigation tubing that fed directly into each column individually from a 100 l tank, filled with secondary wastewater in an adjacent room. Influent wastewater came from the Cayuga Wastewater Treatment Plant in Ithaca, NY. Wastewater was picked up weekly–biweekly in a 1100 l tank and pumped into a 600 l storage tank, with the residual wastewater stored at RT until it was needed. The secondary effluent was then pumped from the 600 l holding tank, through a sand filter to remove suspended solids and into the previously mentioned 100 l tank, that was the source tank for the influent tubing. Influent concentrations of soluble reactive phosphorus were measured before and after the sand filter. The sand filter was box shaped and constructed with PVC sheets, with the following dimensions: $0.6 \times 0.6 \times 1.2$ m. The filter was filled with ≈ 7.5 cm of gravel followed by a geo-textile sheet and 38.1 inches of fine blasting sand (effective diameter 0.45–0.55 mm) and 38.1 inches of anthracite coal (effective diameter 0.9–1.0 mm).

Effluent and influent samples of the columns for phosphorus analysis, were taken from the column every 3 days. The effluent flow rate was measured each time samples were taken, as were measurements of the pressure differential between inflow and outflow. Samples were either analyzed for soluble reactive phosphorus using the ascorbic acid method on the date they were taken, or

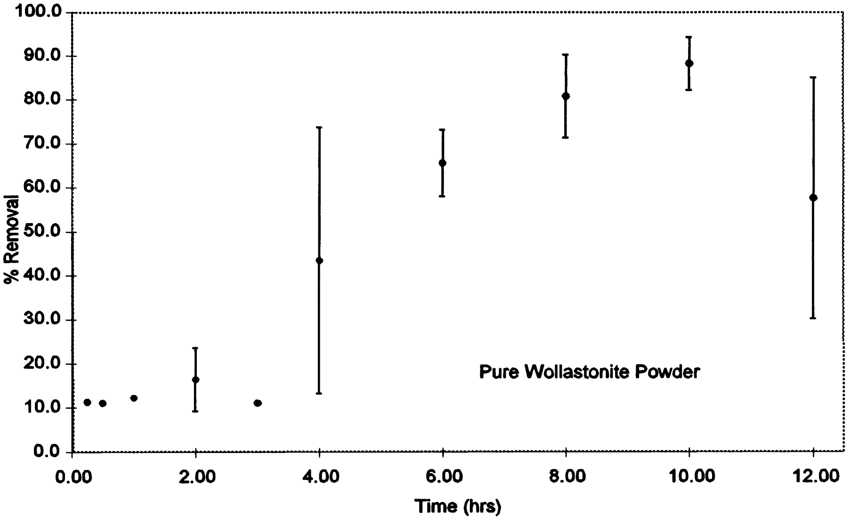

Fig. 2. Time dependence of phosphorus removal.

stored overnight at 4°C for measurement the following day. If it was not possible to measure the samples within 2 days, the samples were stored frozen until they could be analyzed.

Tap water inflow with a high phosphorus concentration ($\approx 5–12$ mg/l), was made by adding potassium phosphate dihydrate (KH_2PO_4) to tap water, fed into two of the columns and sampled as described above.

Eight columns were filled with an 1:1 mixture of wollastonite tailings, the by-product of the mining process and pure wollastonite powder, two were filled with a 3:1 tailings/pure wollastonite mixture and one with tailings alone. Columns were monitored for up to 411 days. The mixture of tailings and pure wollastonite, was created by adding equal volumes of each substrate into a cement mixer and agitating for 15 min. Six columns had a secondary wastewater influent source and two had tap water with added phosphorus (KH_2PO_4). The initial residence time (RT_1) was >40 h in all but two of the columns. The residence time was reduced in some columns after close to 50 days of operation (RT_2) to monitor changes in the effluent concentrations of soluble reactive phosphorus based as a function of residence time. The average residence time was based on measured effluent flow rates using the following equation:

$$T_{r_{\text{ave}}} = \frac{\pi r^2 h \phi}{Q_{\text{ave}}} \qquad (1)$$

where $T_{r_{\text{ave}}}$ is the average residence time (h); Q_{ave} is the average measured flow rate (ml/h); r is the radius of the column (cm); h is the height of the substrate in the column (cm); ϕ is the porosity of the substrate.

The RT_1 and RT_2 of each column, as well as other attributes of the individual columns, are shown in Table 1.

3. Results

3.1. Batch experiments

Time series experiments were done, by mechanically agitating known concentrations of phosphate solution with wollastonite for designated periods of time and then measuring the dissolved phosphate left in solution. Fig. 2 shows the time dependence of phosphorus removal in batch experiments. Ninety percent removal was observed in the first 12 h of the experiment and 98–100% removal was achieved after 72 h of mechanical shaking (data not shown). The data points are averages obtained from three experiments done with initial concentrations of 5 and 10 mg/l and the error bars represent ± 1 S.D.

Table 1
Vertical columns experimental summary[a]

Column	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11
Substrate	1:1 T+P	1:1 T+P	3:1 T+P	3:1 T+P	1:1 T+P	1:1 T+P	1:1 T+P	1:1 T+P	1:1 T+P	1:1 T+P	Tailings
Porosity	0.54	0.54	0.47	0.47	0.54	0.54	0.54	0.54	0.54	0.54	0.34
RT_1 (h)	54	59	22	22	90	52	78	67	70	80	40
Days of Operation	95	141	46	46	46	46	161	161	130	213	46
RT_2 (h)	160	19	15	45	17	17			228	17	23
Days of Operation	213	115	115	115	115	115			83		115
Influent Source	SW	SW	SW	SW	SW	SW	SW	SW	TW	TW	SW

[a] T+P, tailings/pure wollastonite powder; SW, secondary wastewater; TW, tap water/phosphate solution; $RT_{1,2}$, initial and secondary residence times.

The addition of a crystal seed of calcium phosphate was accomplished, by adding wollastonite that had been previously agitated with a phosphate solution for 72 h (98% measured removal) and dried overnight. Time dependence of phosphorus removal in experiments carried out with the seeding process are shown in Fig. 3. After 2 h, 27% of the phosphorus had been removed in the experiment with seeding, versus 16% in the time experiments without seeding. However, net removal in both seeded and non seeded experiments was the same, 80% after 8 h and 90% after 12 h.

3.2. Column experiments

The percent decrease of soluble reactive phosphorus (SP) in secondary wastewater, treated in vertical upflow columns at RT_1 and RT_2 as calculated by Eq. (1), is given in Table 2. The average effluent concentration, S.D. and percent removal are averages over the number of days of operation shown for RT_1 and RT_2. The results shown, permit comparisons of residence time, as well as influent source.

A maximum average removal of 96% was observed in column C9 over a period of 83 days. The longest period of successful removal (> 85%), was observed in column C1. Fig. 4 shows the influent and effluent concentrations of soluble reactive phosphorus in column C1. The secondary wastewater inflow varied between 0.16 and 9.8 mg/l (average is 3.4 mg/l) and the average effluent concentration over a period of 411 days was 0.3 mg/l. Column C1 removed, on average, 89% over the first 95 days of operation and then removed 90% over the next 213 days. The column showed no signs of a decrease in effectiveness over the duration of this experiment. Removals of soluble reactive phosphorus > 80% were achieved in nine out of 11 vertical upflow columns, with average effluent concentrations of SP ranging from 0.14 to 0.50 mg/l (averaging 0.28 mg/l).

Fig. 5 shows the influent and effluent concentration of soluble reactive phosphorus in the vertical column, filled only with wollastonite tailings, without the addition of pure powder wollastonite. The tailings column was started at an RT_1 of 40 h. The residence time was decreased to 30 h after 50 days of operation and then increased after ≈ 170 days of operation to over 100 h. The

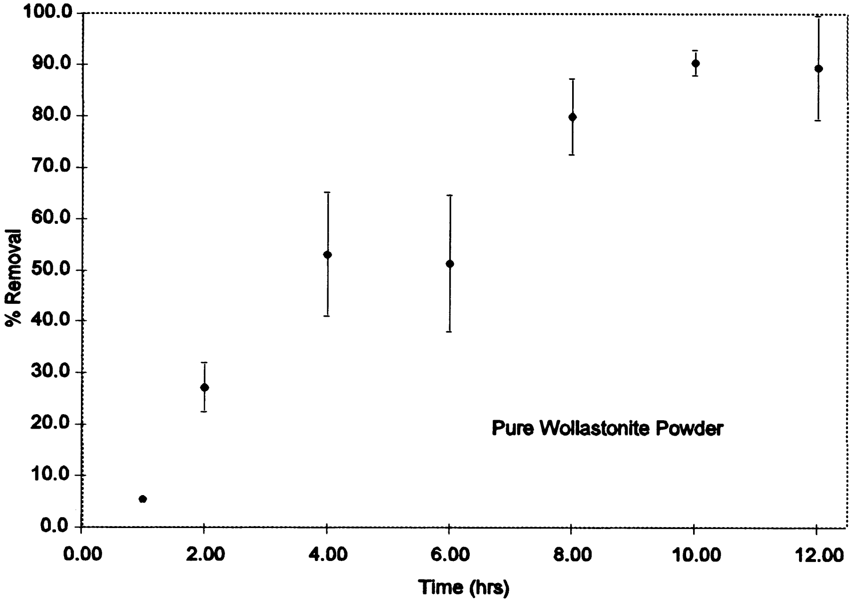

Fig. 3. Time dependence of phosphorus removal with seeding.

Table 2
Soluble reactive phosphorus (SP) removal in vertical flow columns[a]

Column	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11
Substrate	1:1 T+P	1:1 T+P	3:1 T+P	3:1 T+P	1:1 T+P	1:1 T+P	1:1 T+P	1:1 T+P	1:1 T+P	1:1 T+P	Tailings
RT_1 (h)	54	58	26	22	91	49	71	63	84	93	40
Average SP (mg/l)	0.38	0.24	0.65	0.68	0.14	0.15	0.28	0.31	0.29	0.18	0.19
(S.D.)	(0.1)	(0.11)	(0.28)	(0.33)	(0.05)	(0.06)	(0.48)	(0.59)	(0.21)	(0.12)	(0.21)
SP removal (%)	89	91	53	51	90	89	86	85	85	87	84
RT_2 (h)	143	19	15	45	17	18			179	15	30
Average SP (mg/l)	0.21	1.86	2.54	2.07	2.23	2.17			0.25	0.57	1.41
(S.D.)	(0.10)	(1.5)	(1.47)	(1.27)	(1.80)	(1.7)			(0.10)	(0.23)	(1.09)
SP removal (%)	90	49	36	43	39	40			96		66
Influent source	SW	SW	SW	SW	SW	SW	SW	SW	TW	TW	SW

[a] T+P, tailings/pure wollastonite powder; SW, secondary wastewater; TW, tap water/phosphate solution; $RT_{1,2}$, initial and secondary residence times.

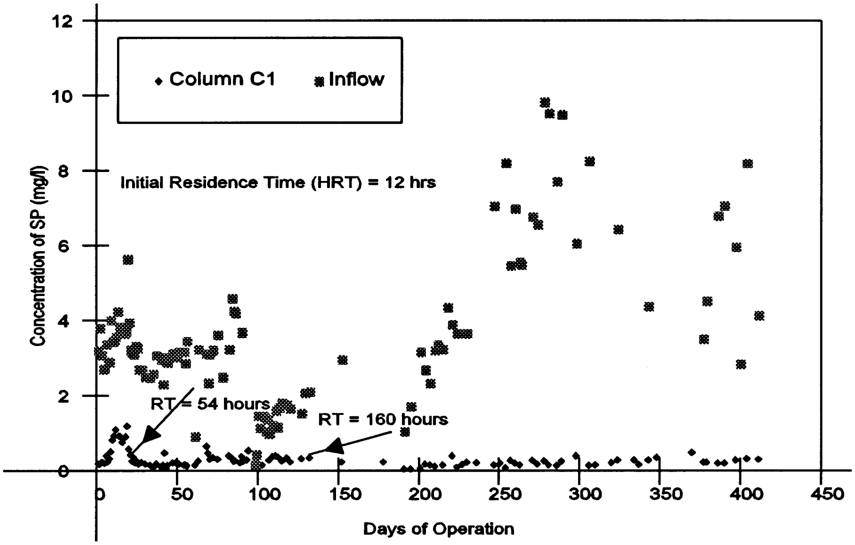

Fig. 4. Effluent concentrations of soluble reactive phosphorus in column C1.

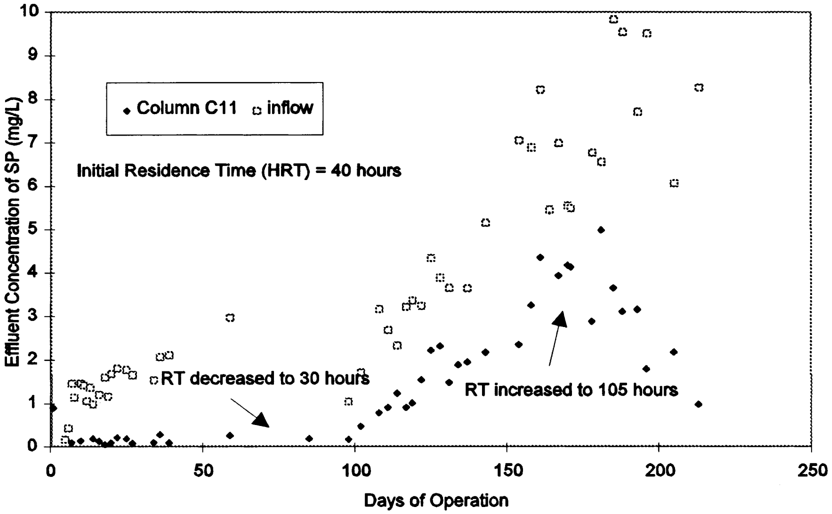

Fig. 5. Effluent concentrations of soluble reactive phosphorus in column C11, wollastonite tailings.

effluent concentrations, reflect these changes in the column residence time (Fig. 5). Similar results were observed in all other wastewater influent columns. Columns receiving tap water influent (columns C9 and C10) maintained removal percentages > 80% regardless of residence time (Table 2).

4. Discussion

4.1. Batch experiments

Phosphorus removal in batch experiments has been attributed to adsorption in studies where significant removal by pumice rock was observed in 60 min (Nur Onar et al., 1996) and where removal by river sediments occurred within 10 min (Fox et al., 1989). The removal reaction proceeded much more slowly in this experiment, although significant removal was observed on a scale of h. P removal associated with complexation and precipitation of hydroxyapatite, occurred in < 24 h in an experiment by Mann and Bavor (1993). Although 10% removal of P was observed in < 2 h in this experiment, the most significant fractional removal occurred between 2 and 8 h. Hundal (1988) studied phosphorus removal by a Narrabi medium clay loam and found results similar to this study, describing the removal in the first 6 h as nucleation of calcium phosphate on soil surfaces and associated the second reaction (up to 24 h) with precipitation of amorphous calcium phosphate over the nucleated sites. Based on the kinetics of the reaction(s) taking place in this experiment (Fig. 2, Fig. 3), it does not appear that removal can be fully attributed to rapid adsorption reactions, but may indicate either a combination of both adsorption and a more complex reaction such as surface precipitation or a simply mineral dissolution and subsequent precipitation of phosphate without the influence of adsorption.

Ferguson (1971) showed that the time delay before phosphorus removal, occuring in a supersaturated solution can be reduced, with the addition of a crystal seed of precipitated calcium phosphate. The increased rate of calcium phosphate precipitation is attributed to the elimination of the induction period of crystal growth. The increased rate of P removal in the seeding experiments in this study (Fig. 3) indicates that precipitation may be occurring. Furthermore, an increased rate of removal after seeding would not be expected in a purely adsorptive process unless the specific surface area were somehow greatly increased by this process.

4.2. Column experiments

It has been shown repeatedly that phosphorus removal from soil exhibits both rapid and slow stages (Ryden and Pratt, 1980; Nur Onar et al., 1996). This is visible in the batch experiments (Fig. 2). A similar trend was found in the column experiments after a data point at 72 h is included in the graph (Fig. 6). The relationship between residence time and percent removal in the vertical columns is shown in Fig. 7. The data shown represent average removal at RT_1 and RT_2 in seven different columns. The residence time was not changed in two columns and, therefore, there is only an RT_1 for each of those, resulting in a total of 16 data points. The data from the tap

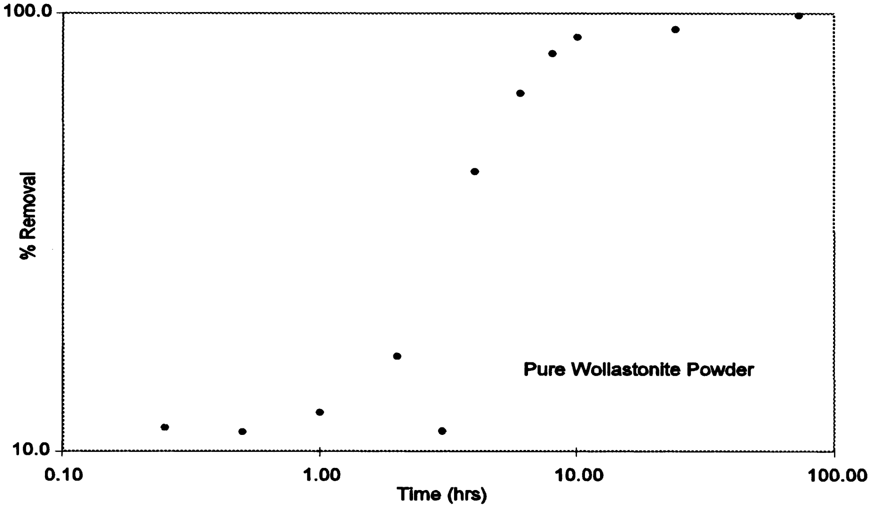

Fig. 6. Data from Fig. 2 plotted on a log scale with a data point at 72 h included.

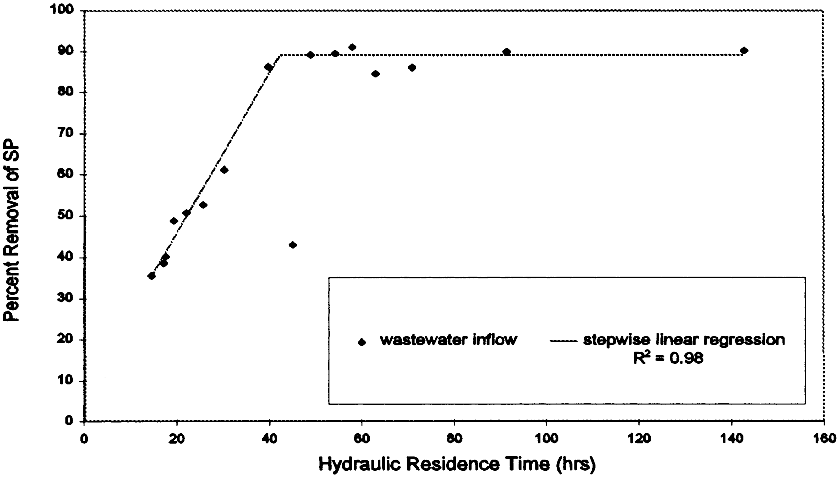

Fig. 7. Comparison of residence time and percent removal of soluble reactive phosphorus.

water columns is not included. Percent removal increases linearly with residence time until ≈ 43 h. The fractual removal appears to level off beyond that time.

The initial rapid reaction is typically described as adsorption, but can also be attributed to the formation of calcium phosphates of high solubility (Frossard et al., 1995). The subsequent slower reaction has been described as either chemical precipitation or incorporation of the adsorbate into the solid matrix (McGlathery et al., 1994). Sposito (1984) indicated that the rapid phase usually lasts for < 50 h and the slow stage can continue beyond 50 days. This is in agreement with the data from this experiment, as removal continued at a rapid rate up to ≈ 43 h (the first stage) and then appeared to level off (Fig. 6). The results of this experiment indicate that, in order to achieve maximum removal, the residence time in the vertical columns must be long enough to achieve at least the second (slow) stage of phosphorus removal.

The observed result, that the column filled with wollastonite tailings by themselves, followed the same removal trend as the tailings/pure powder mixtures (Fig. 5) has significant economical consequences. The cost of the pure wollastonite powder is \$308/ton compared to \$3/ton for the tailings by themselves. Future experiments will include replicates of columns filled with wollastonite tailings, at lengthy residence times (> 40 h).

The relationship between increasing influent concentrations of SP and percent removal in vertical column C1 is shown in Fig. 8. The residence time in the column was initially 54 h, but was increased to 160 h just before a period of increased influent concentrations of soluble reactive phosphorus. While the effluent concentration increased in all other columns (residence times varying from 17 to 78 h) with an increase in influent concentration, the average effluent concentration in column C1 actually decreased by 0.13 mg/l. The same relationship was observed in tap water influent columns, but was not seen in any of the other wastewater influent columns.

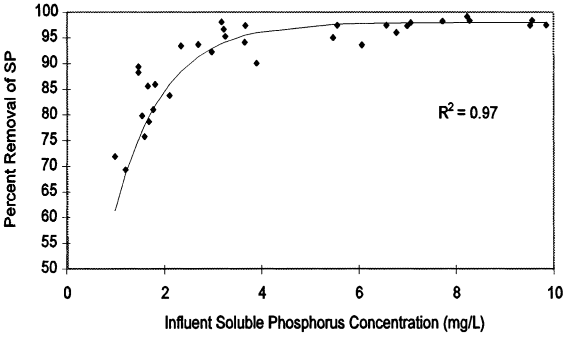

Fig. 8. Relationship between increasing influent concentration and percent removal of SP.

The excellent removal observed in tap water columns (regardless of residence time) may be attributable, in part, to the form of phosphate in solution. The chemical phosphorus, added to the tap water influent source was potassium phosphate monobasic (KH_2PO_4). This salt is a strong electrolyte and will dissociate in solution producing $H_2PO_4^-$, HPO_4^{-2} and PO_4^{-3} ions immediately available for reaction. The wastewater phosphorus will be a combination of ortho- and polyphosphates, as well as organic phosphorus. Prolonged contact with micro-organisms in wastewater, will cause polyphosphates to hydrolyze to orthophosphates and that, along with competition with other compounds in the wastewater, may cause a delay in the removal process. An alternate possibility is that biofilm coatings formed in columns receiving wastewater input altered the wollastonite surface adsorptive properties and/or decreased the rate at which wollastonite dissolved to produce the Ca^{2+} that reacted with the phosphate species from a precipitate. Although the rapid and slow stages of removal observed in wastewater influent columns were not observed in tap water columns, it is possible that they still exist, but at residence times shorter than studied experimentally.

5. Conclusion

Vertical flow columns filled with a 1:1 mixture of wollastonite powder and wollastonite tailings are shown to be an efficient means of achieving soluble reactive phosphorus removal, from secondary municipal wastewater. Wollastonite tailings by themselves also show promise as a more economic means of obtaining removal in constructed wetland ecosystems, although further research would be necessary to verify the results found in this study. Residence time is clearly a significant factor in optimizing phosphorus removal in the design of full-scale wetland systems. The highest percent removal was achieved at residence times >40 h. The relationship between percent removal and residence time was exhibited as two phases of soluble reactive phosphorus removal. The first suggests a rapid reaction, that is attributed to adsorption or the formation of calcium phosphates of high solubility and the second, slower reaction, suggests the result from either chemical precipitation or incorporation of the adsorbate into the solid matrix. Phosphorus removal by wollastonite substrate with a tap water inflow, was not as sensitive to residence time as with wastewater. This difference was attributed to interference with other compounds found in wastewater or to biofilm modification of the column substrate. Batch experiments showed 90% removal of phosphorus after 12 h of agitation and precipitation of calcium phosphates was indicated by an increased removal rate in seeding experiments. In summary, wollastonite tailings are an attractive ecotechnological alternative to chemical treatment methods for removing phosphorus from a secondary treated system. Other possible eco-engineering uses of wollastonite are as a substrate for dairy milk house wetland systems and for individual leach field application, in areas with shallow soils near open water bodies.

References

Agbenin, J.O., 1996. Phosphorus sorption by three cultivated Savanna alfisols as influenced by pH. Fert. Res. 44, 107–112.

APHA, AWWA and WPCP, 1985. Standard Methods for Examination of Water and Wastewater, 16th ed. American Public Health Association, Washington, DC.

Brooks, A.S., 1997. Phosphorus Removal by Wollastonite: A Constructed Wetland Substrate. Unpublished MS Thesis. Department of Agricultural and Biological Engineering, Cornell University, Ithaca, NY.

Buckley, M., 1997. NYCO Minerals Inc., 124 Mountain View Drive, Willsboro, NY 12996. Personal communications.

Corrigan, N., 1993. Selection Of Substrate For Phosphorus Adsorption In Artificially Constructed Wetlands. Unpublished National Science Foundation/Research Experience for Undergraduates Report. Department of Agricultural and Biological Engineering, Cornell University, Ithaca, NY.

EPA, 1987. Phosphorus Removal: Design Manual. Environmental Protection Agency, Washington DC.

Fennessy, M.S., Mitsch, W.J., 1989. Design and use of wetlands for renovation of drainage from coal mines. In: Mitsch, W.J., Jørgensen, S.E. (Eds.), Ecological Engineering. An Introduction to Ecotechnology. Wiley, NY.

Ferguson, J.F., 1971. Effect of crystal seeding on rate of calcium phosphate precipitation. Water Res. 5, 369–381.

Fox, I., Malati, M.A., Perry, R., 1989. The adsorption and release of phosphate from sediments of a river receiving sewage effluent. Water Res. 23, 725–732.

Frossard, E., Brossard, M., Hedley, M.J., Metherell, A., 1995. Reactions controlling the cycling of P in soils. In: Tiessen, H. (Ed.), Phosphorus in the Global Environment. Wiley, Chichester, UK.

Geohring, L.D., Steenhuis, T.S., Corrigan, N., et al., 1995. Specialized substrates for phosphorus removal with constructed wetlands. In: Campbell, K.L. (Ed.), Versatility of Wetlands in the Agricultural Landscape. ASAE Publication 70IP0995. American Society of Agricultural Engineers, St. Joseph, MI, pp. 607–617.

Greenway, M., Woolley, A., 1999. Constructed wetlands in Queensland: Performance efficiency and nutrient bioaccumulation. Ecol. Eng. 12, 39–56.

Hillbricht-Ilkowska, A., Ryszkowski, L., Sharpley, A.N., 1995. Phosphorus transfers and landscape structure: riparian sites and diversified land use patterns. In: Tiessen, H. (Ed.), Phosphorus in the Global Environment. Wiley, Chichester, U.K.

House, C.H., Broome, S.W., Hoover, M.T., 1994. Treatment of nitrogen and phosphorus by a constructed upland-wetland wastewater treatment system. Water Sci. Tech. 29, 177–184.

Hundal, H.S., 1988. A mechanism of phosphate adsorption on Narrabri medium clay loam soil. J. Agr. Sci. 111, 155–158.

Iannou, A., Dimirkou, A., Doula, M., 1994. Phosphate sorption by calcium-bentonite as described by commonly used isotherms. Comm. Soil Sci. Plant Anal. 25, 2299–2313.

Jenssen, P.D., Maehlum, T., Krogstad, T., 1993. Potential use of constructed wetlands for wastewater treatment in northern environments. Water Sci. Tech. 28, 149–157.

Kadlec, R.H., Knight, R.L., 1996. Treatment Wetlands. Lewis Publishers, Boca Raton, FL.

Kern, J., Idler, C., 1999. Treatment of domestic and agricultural wastewater by reed systems. Ecol. Eng. 12, 13–26.

Mann, R.A., 1990. Phosphorus removal by constructed wetlands: substratum adsorption. In: Cooper, P.F., Findlater, B.C. (Eds.), Constructed Wetlands in Water Pollution Control: Advances in Water Pollution Control. Pergamon Press, Oxford, pp. 97–105.

Mann, R.A., Bavor, H.J., 1993. Phosphorus removal in constructed wetlands using gravel and industrial waste substrata. Water Sci. Tech. 27, 107–113.

McGlathery, K.J., Marino, R., Howarth, R.W., 1994. Variable rates of phosphate uptake by shallow marine carbonate sediments: Mechanisms and ecological significance. Biogeochemistry 25, 127–146.

Mitsch, W.J., Jørgensen, S.E. (Eds.), 1989. Ecological Engineering. An Introduction to Ecotechnology. Wiley, NY.

Nur Onar, A., Balkaya, N., Akyuz, T., 1996. Phosphate removal by adsorption. Env. Tech. 17, 207–213.

Reed, S.C., Brown, D.S., 1992. Constructed wetland design: the first generation. Water Env. Res. 64, 776–781.

Ryden, J.C., Pratt, P.F., 1980. Phosphorus removal from wastewater applied to land. Hilgardia 48, 1–36.

Sposito, G., 1984. The Surface Chemistry of Soils. Oxford University Press, New York, NY.

Verhoeven, J.T.A., Meuleman, A.F.M., 1999. Wetlands for wastewater treatment: opportunities and limitations. Ecol. Eng. 12, 5–12.

Watson, J.T., Reed, S.C., Kadlec, R.H., Knight, R.L., Whitehouse, A.E., 1989. Performance expectations and loading rates for constructed wetlands. In: Hammer, D.A. (Ed.), Constructed Wetlands for Waste Water Treatment. Lewis Publishers, Chelsea, MI, pp. 319–351.